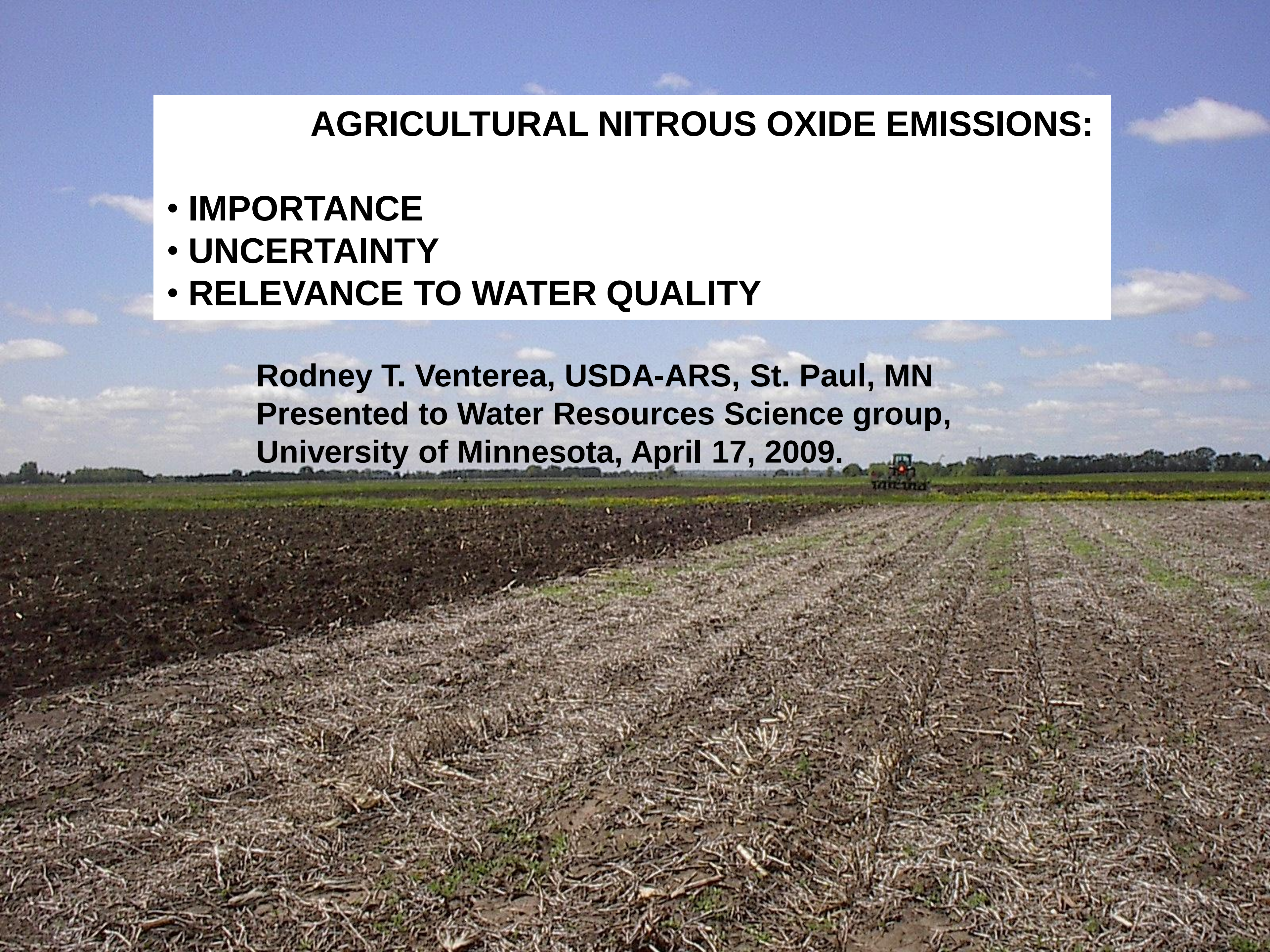
AGRICULTURAL NITROUS OXIDE EMISSIONS:

- **IMPORTANCE**
- **UNCERTAINTY**
- **RELEVANCE TO WATER QUALITY**

Rodney T. Venterea, USDA-ARS, St. Paul, MN
Presented to Water Resources Science group, University of Minnesota, April 17, 2009.



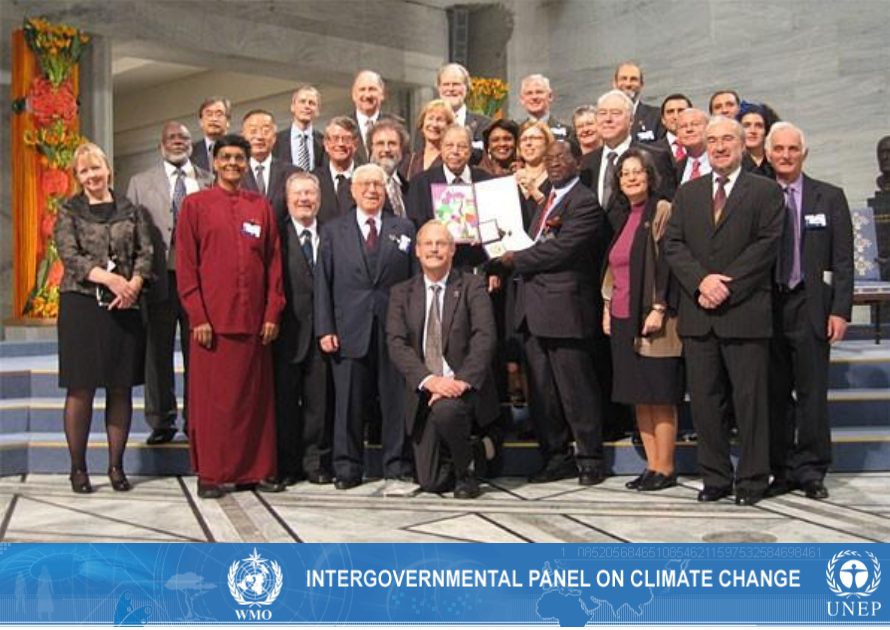
EPA to Clear the Way for Regulation of Warming Gases

April 17, 2009
By JOHN M. BRODER

WASHINGTON — The Environmental Protection Agency on Friday formally declared carbon dioxide and five other heat-trapping gases to be pollutants that threaten public health and welfare, setting in motion a process that for the first time in the United States will regulate the gases blamed for global warming.

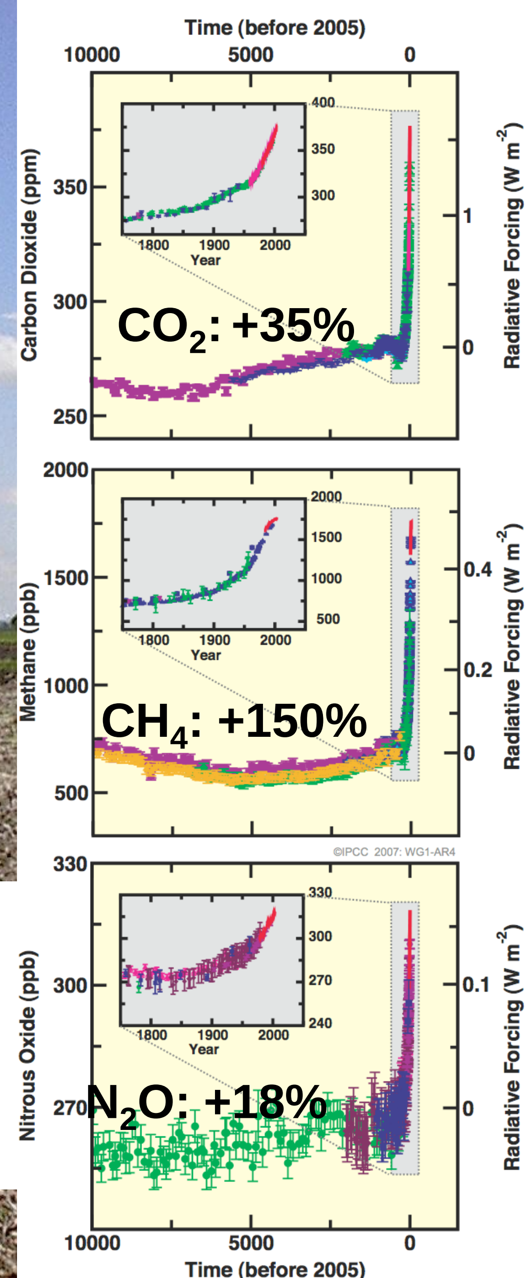
The E.P.A. said the science supporting its so-called endangerment finding was “compelling and overwhelming.”

The New York Times



Established by WMO and UNEP (1988)
Nobel Peace Prize (2007)

Changes in Greenhouse Gases from ice-Core and Modern Data



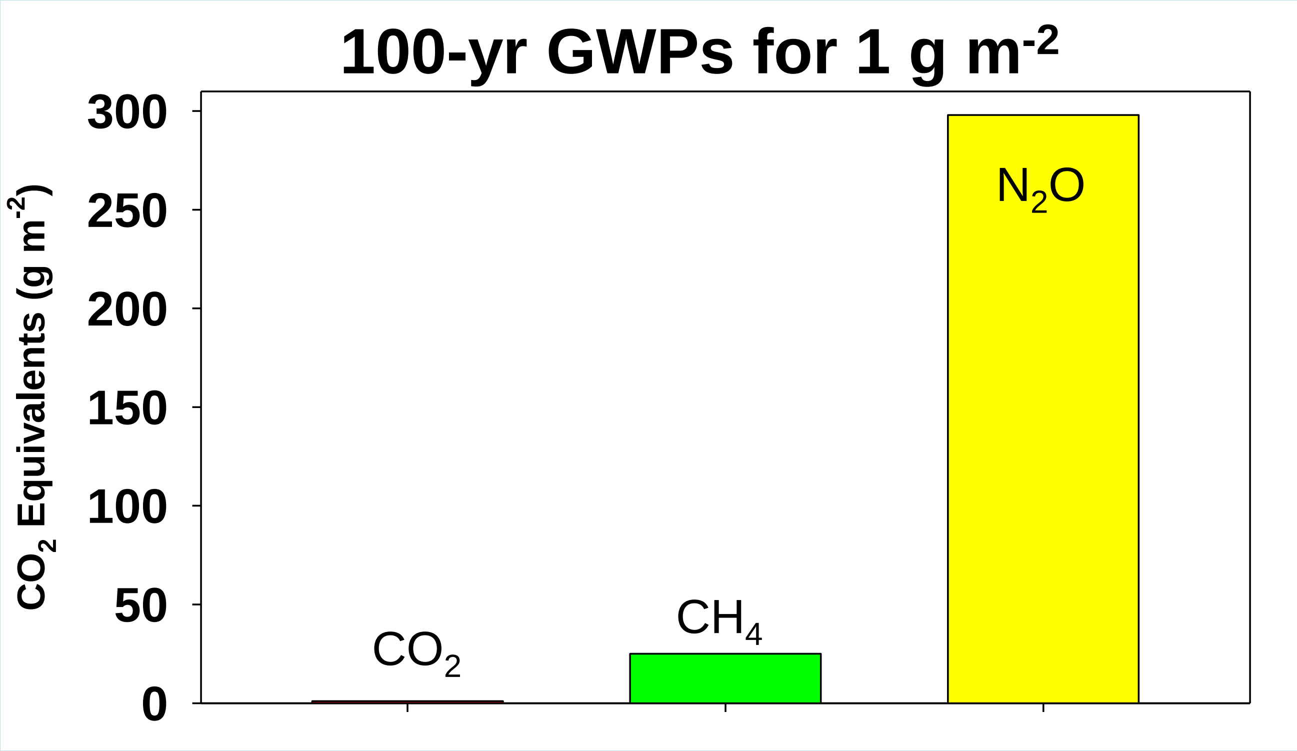
IPCC, 2007.

Atmospheric Concentrations over past 10,000 years:

Nitrous oxide (N_2O):
- Smallest relative increase (+18%)
- Mainly due to fertilizer use

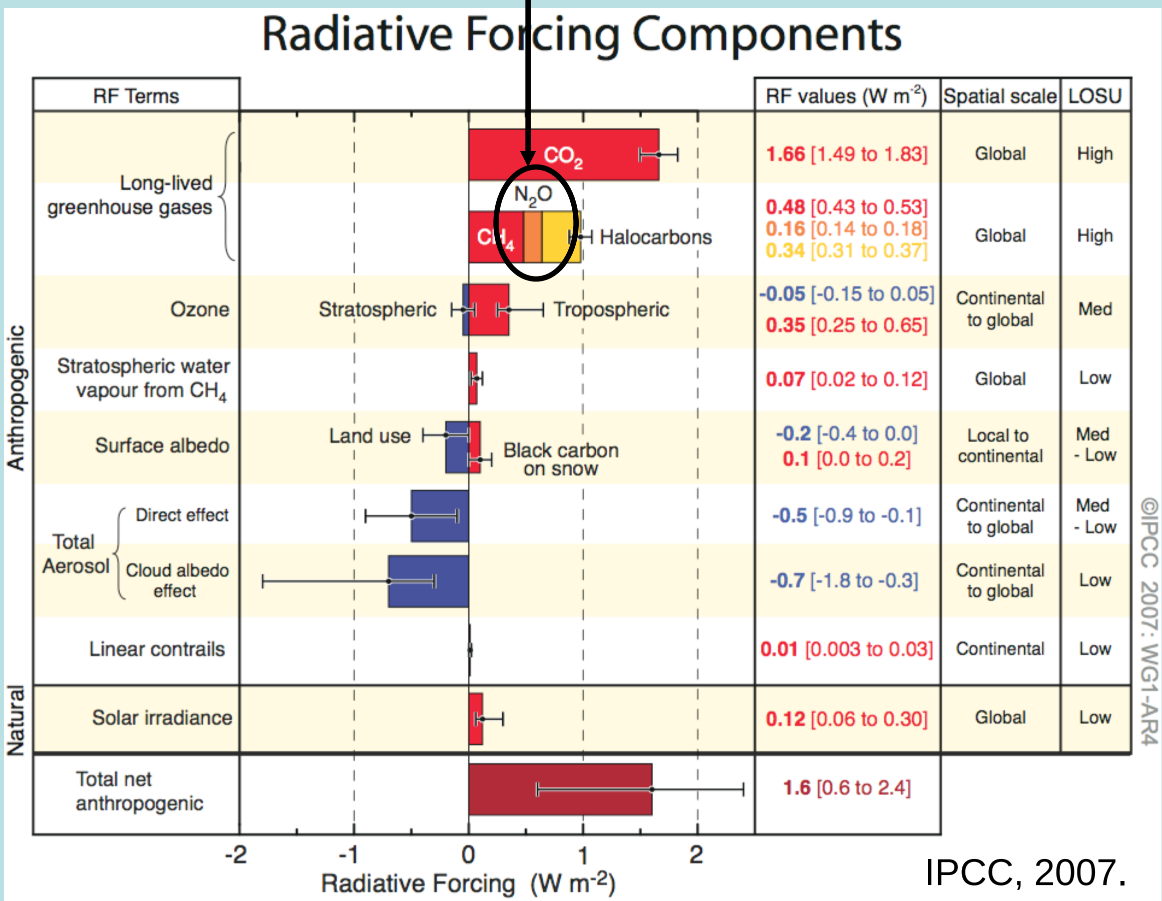
GLOBAL WARMING POTENTIAL

The radiative forcing of a given mass of GHG relative to CO_2 over a given time horizon:(i) atmospheric lifetime, and (ii) effectiveness in absorbing outgoing thermal infrared radiation.



CONTRIBUTION TO ANTHROPOGENIC GREENHOUSE GASES

N_2O = 10% of CO_2



IPCC, 2007.

WHY CARE ABOUT N_2O ?

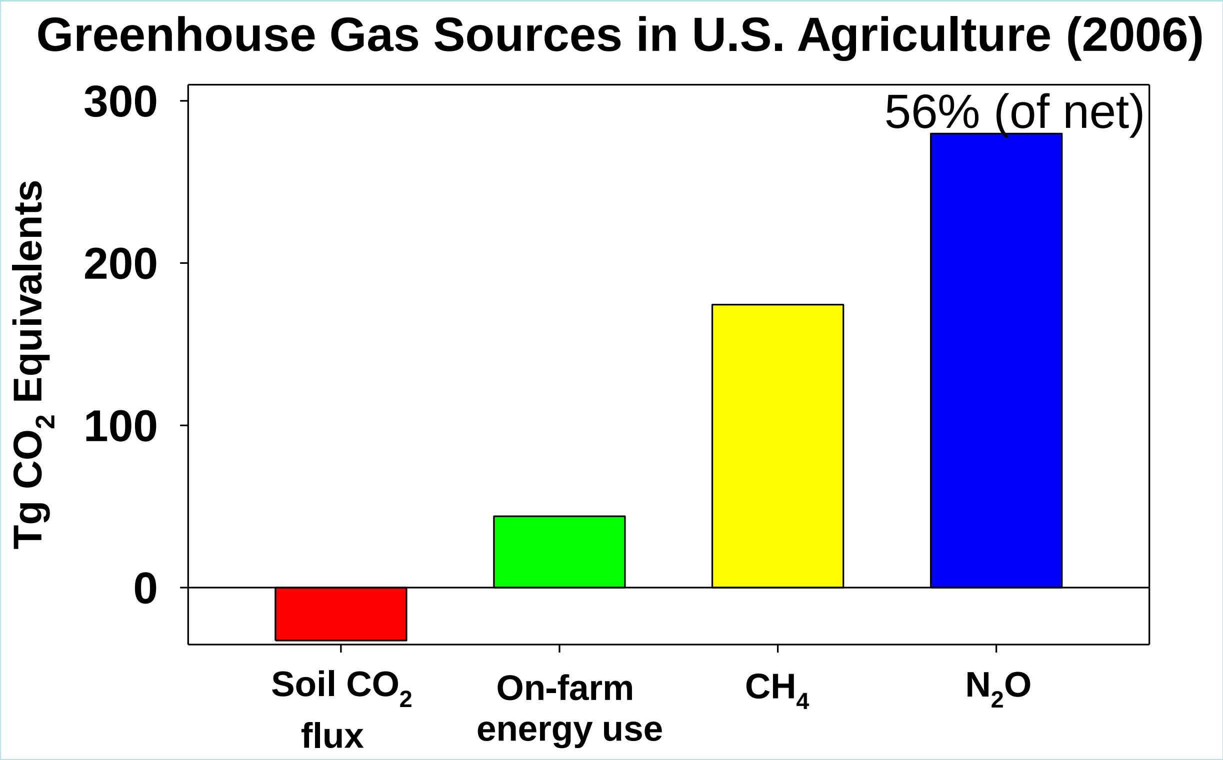
1. Widespread use of low-CO_2 energy technologies is not expected for 30 to 50 years. Other GHG reductions are needed now.

2. Due to high Global Warming Potential of N_2O relative to C_2O, N_2O is often the greatest single GHG source for any particular system:

- Feasibility of biofuels
- Life cycle analysis of different management practices (e.g., reduced tillage, intensifying rotations, organic farming, cover crops, etc.)
- Potential for selling N_2O reduction mgmt as “Carbon Credits”

3. Reduction in N_2O emissions will also have water quality benefits.

WHY CARE ABOUT N_2O ?



USEPA, 2008.

WHY CARE ABOUT N_2O ?

Stephen Chu
Secretary of Energy
Nobel Prize Physics (1997: Development of methods to cool and trap atoms with laser light)

"We're in the great ship Titanic (the Earth), and it's going to take a half century to turn the ship. Ultimately some form of solar energy will be the solution. But on the time scale of 30 years, we have to work on capture and storage of carbon (and CO_2 equivalents)." *– Newsweek, 4/11/09*

"Let me just say there's 101 ways to do biofuels wrong, and a couple of ways to do it right." - *Chinadialogue, 3/24/09*

"There needs to be a second Green Revolution, because we are not doing agriculture in a sustainable way. There's a huge greenhouse-gas problem. There's a water pollution problem. And the farmer doesn't pay for the … nitrate and all the nitrous oxide being generated." - *Chinadialogue, 3/24/09*

HOW MUCH N_2O DOES AGRICULTURE EMIT?

Top-down analysis: Can be done only at Global Scale.

Based on assessment of global atmospheric N_2O concentrations, sources and sinks.

Bottom-up analysis: Can be done at any scale

Field, farm, county, state, national….

Estimate fluxes for given land use (via measurement or model).

Multiply flux by respective land area.

Sum up all contributions.

TOP-DOWN ANALYSIS OF AGRICULTURAL N_2O EMISSIONS

Paul Crutzen
Atmospheric Chemist
Nobel Prize Chemistry (1995: Role of Nitrogen Oxides in Regulating Stratospheric Ozone)

In stratosphere: $N_2O \rightarrow NO$

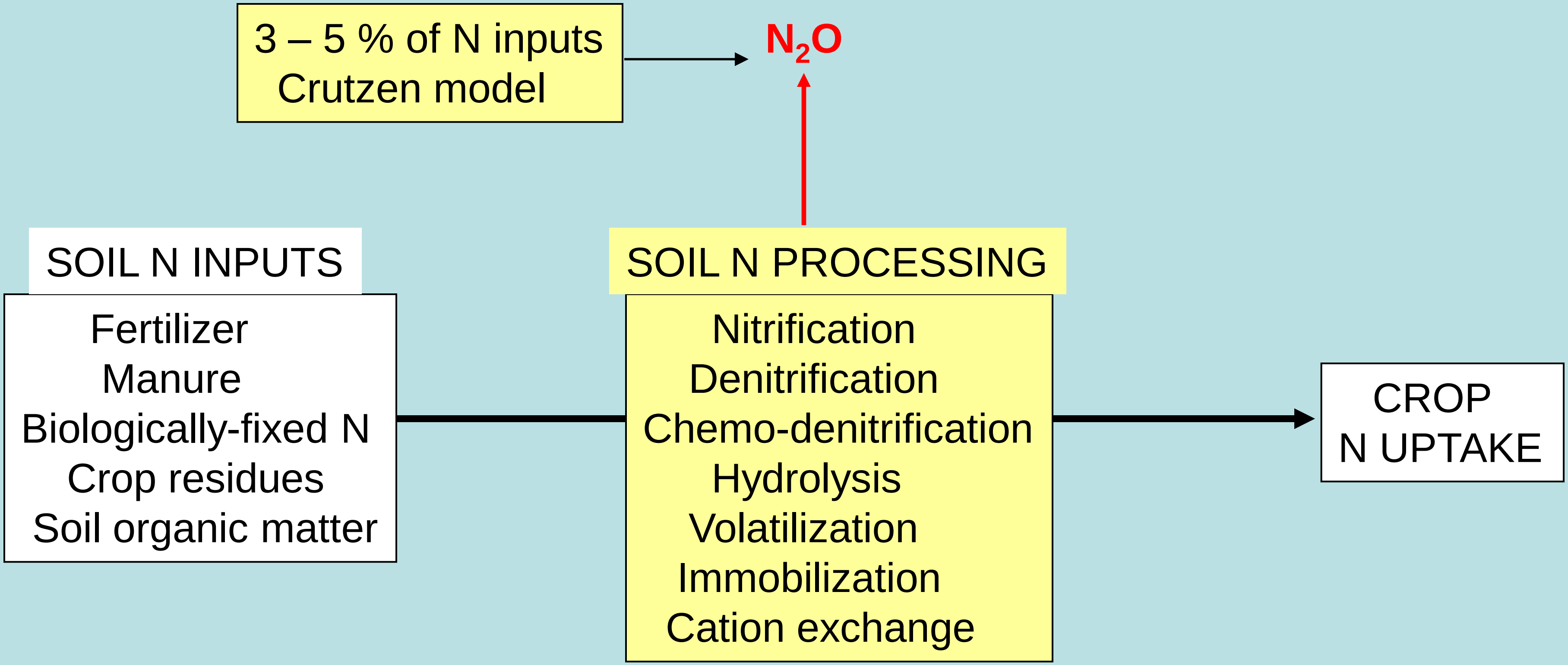
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$
$O_3 + uv \rightarrow O_2 + O$

Net result: $2\ O_3 \rightarrow 3\ O_2$

- Used current and historical N_2O concentrations to derive values for global N_2O sinks and sources.

- Conclusion: Between 3% and 5% of N inputs to agricultural soil is converted to N_2O.

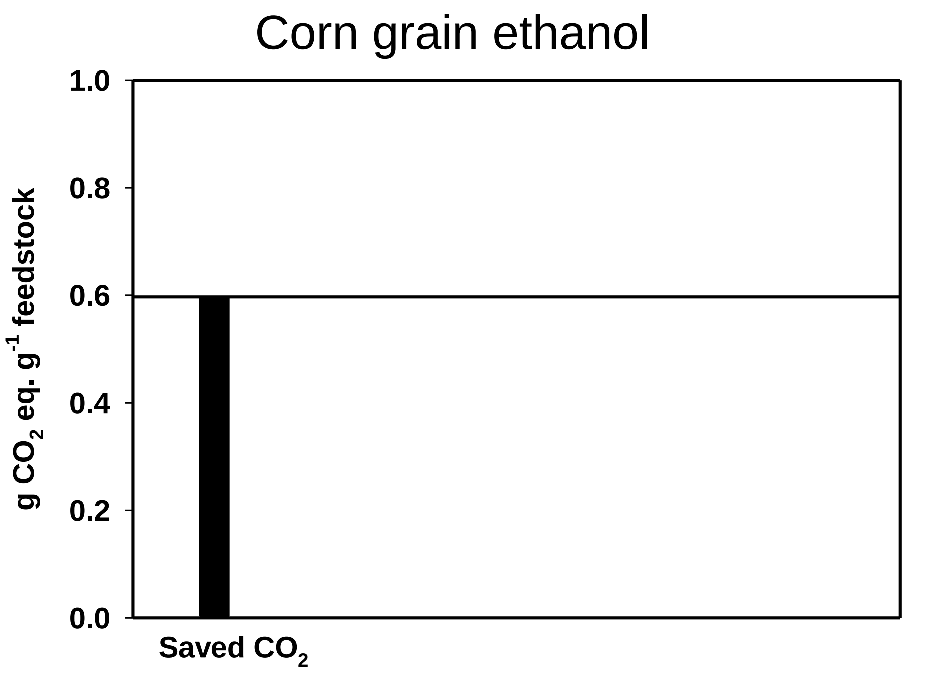
CONCEPTUAL MODEL OF SOIL N_2O EMISSIONS



Application of top-down estimates to analysis of biofuel production

Comparison of fossil fuel CO_2 displaced by biofuel to N_2O emitted during production of biofuel crop

$$Saved\,CO_2 = \left(\frac{0.44g\ C\ \ feedstock}{g\ \ feedstock}\right)\left(\frac{0.37g\ C\ in\ biofuel}{g\ C\ \ feedstock}\right)\left(\frac{44g\ CO_2}{12g\ C}\right)$$



Crutzen et al. (2008)

Application of top-down estimates to analysis of biofuel production

$$N_2O\ emitted = \left(\frac{0.015g\ N\ feedstock}{g\ feedstock}\right)\left(\frac{g\ N\ applied}{0.40g\ N\ feedstock}\right)\left(\frac{g\ N_2O}{g\ N\ applied}\right)\left(\frac{298g\ CO_2}{g\ N_2O}\right)\left(\frac{44g\ N_2O}{28g\ N}\right)$$

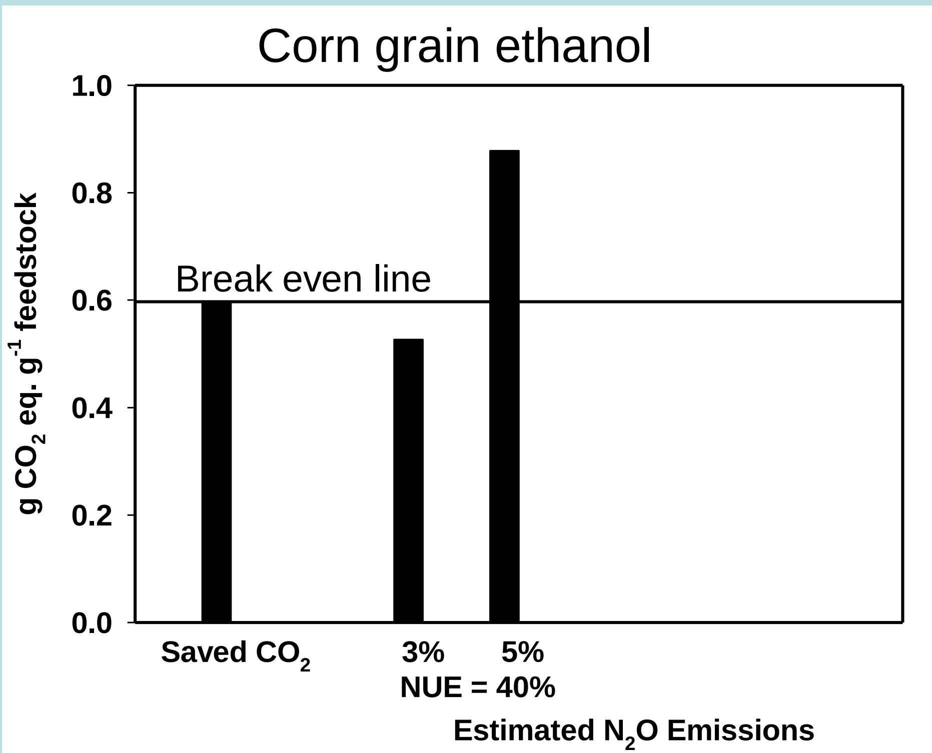
Grain N content

NUE^{-1}

3-5%

GWP

Molar conversion



Crutzen et al. (2008)

Application of top-down estimates to analysis of biofuel production

$$N_2O\ emitted = \left(\frac{0.015g\ N\ \ feedstock}{g\ \ feedstock}\right)\left(\frac{g\ N\ applied}{0.50g\ N\ \ feedstock}\right)\left(\frac{g\ N_2O}{g\ N\ applied}\right)\left(\frac{298g\ CO_2}{g\ N_2O}\right)\left(\frac{44g\ N_2O}{28g\ N}\right)$$

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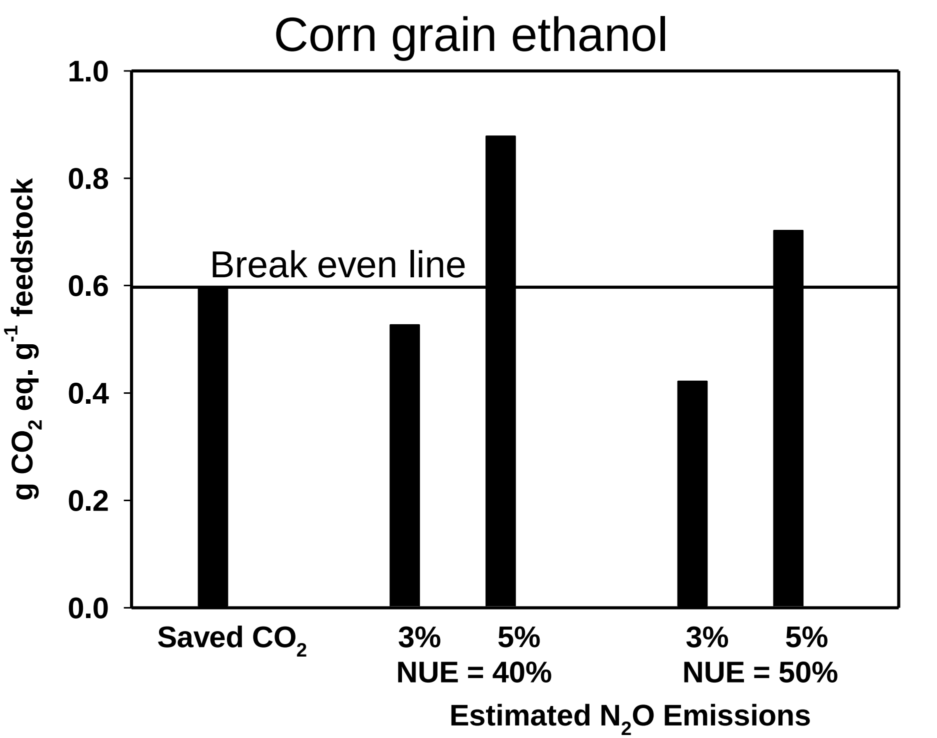

<u>Conclusion</u>

N_2O emissions alone will negate much or all of the GHG benefit of corn grain ethanol

Crutzen et al. (2008)

Application of top-down estimates to analysis of biofuel production

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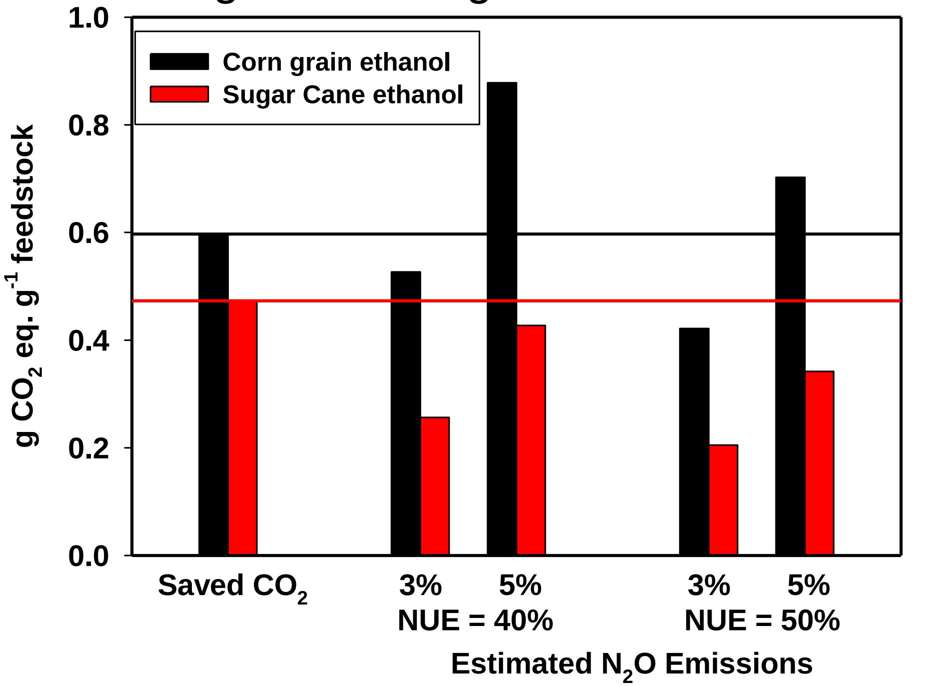
Corn grain vs. Sugar Cane ethanol



<u>Conclusion</u>

N_2O emissions alone will negate much or all of the GHG benefit of corn grain ethanol

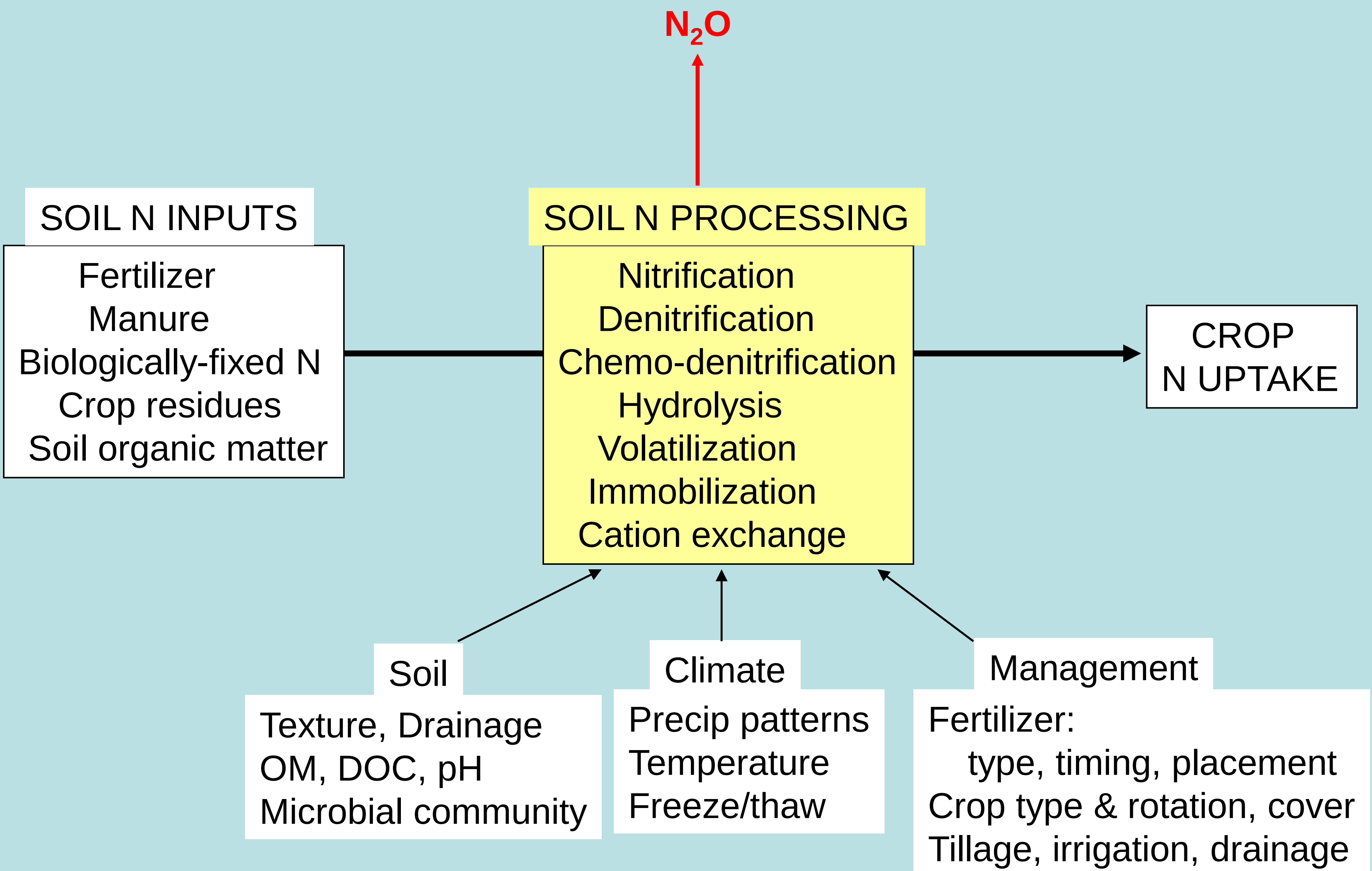
Crutzen et al. (2008)

Major Limitations of Crutzen et al (2008)

1. Re: Biofuels – Is not a complete Life Cycle Analysis. E.g., does not consider fuel usage for biomass production, or energy value of co-products.

2. Assumes that any particular cropping system adheres to the 3-5% N_2O production ratio. I.e., does not account for variation due to climate, soil, or management effects.

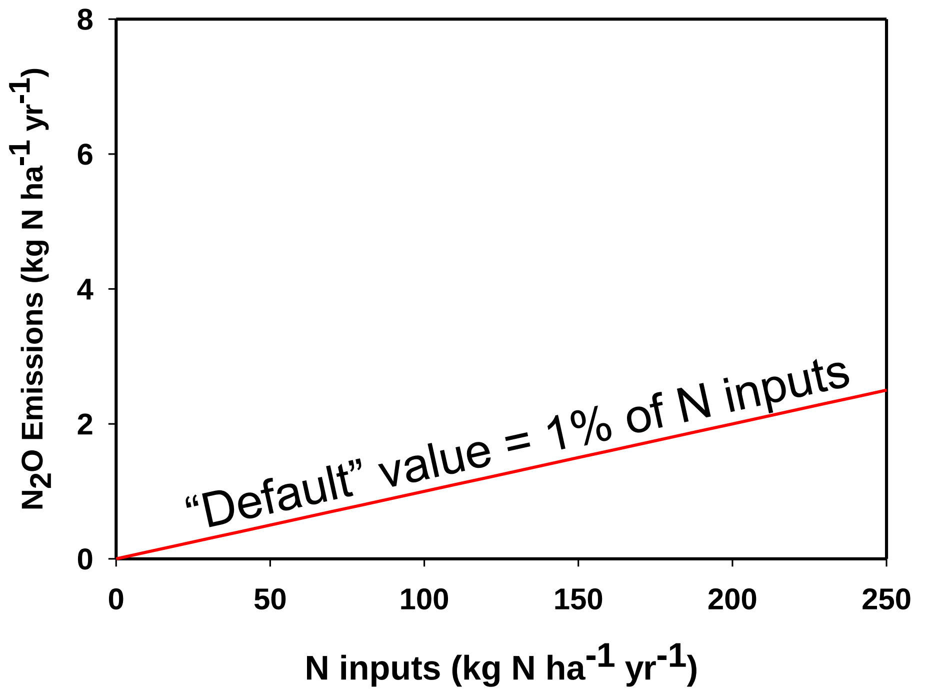
CONCEPTUAL MODEL OF SOIL N_2O EMISSIONS



Several factors will affect fraction of N inputs converted to N_2O for a particular system

Measurements of Soil N_2O Emissions

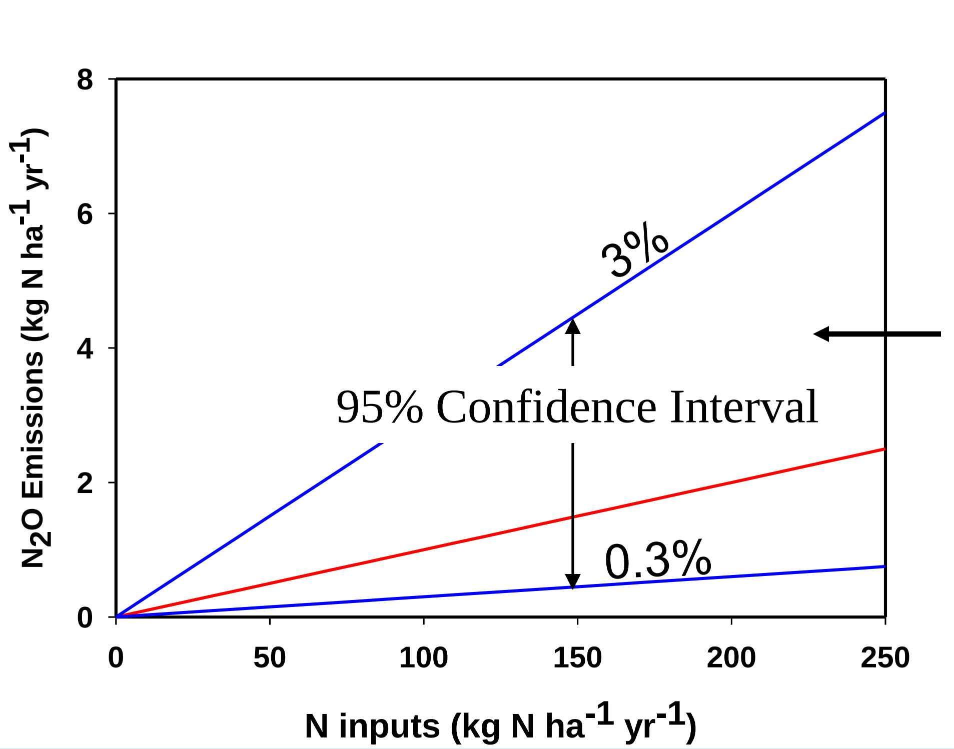
- Hundreds of field studies in past 3 decades across the world:
  - IPCC developed guidelines to estimate emissions based on N inputs
  - Mean or "best estimate" is 1% of N inputs converted to N_2O



IPCC, 2006

Measurements of Soil N_2O Emissions

- Wide variation in the proportionality among the studies
    - 95 % CI varies by an order of magnitude: 0.3 to 3% of inputs
    - The upper limit is on the low end of the Crutzen estimate



This is only the “Direct” N_2O emissions

IPCC, 2006

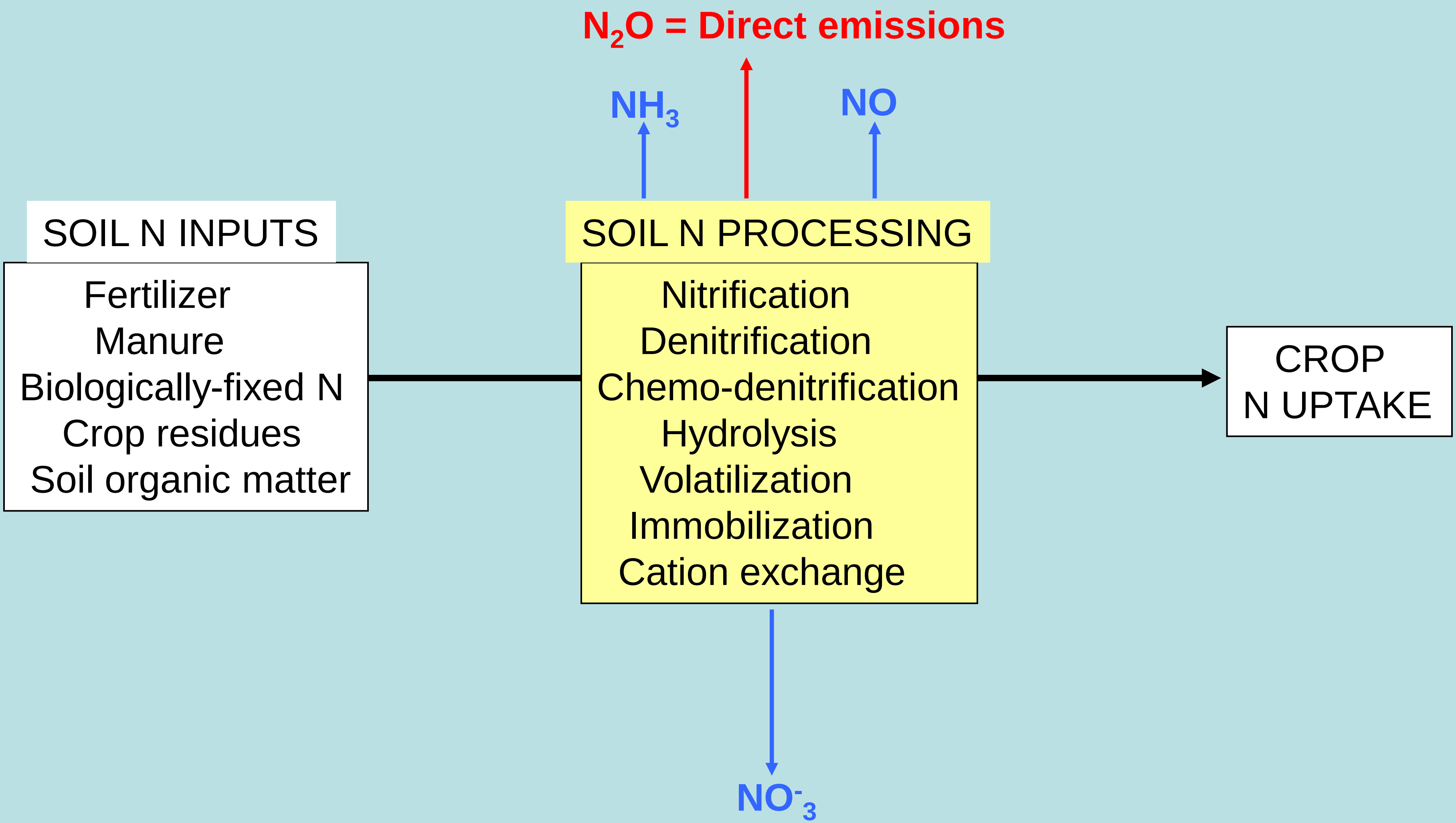
Direct versus Indirect N_2O Emissions

- Direct emissions: N_2O that is emitted from the cropped field as N_2O directly to the atmosphere

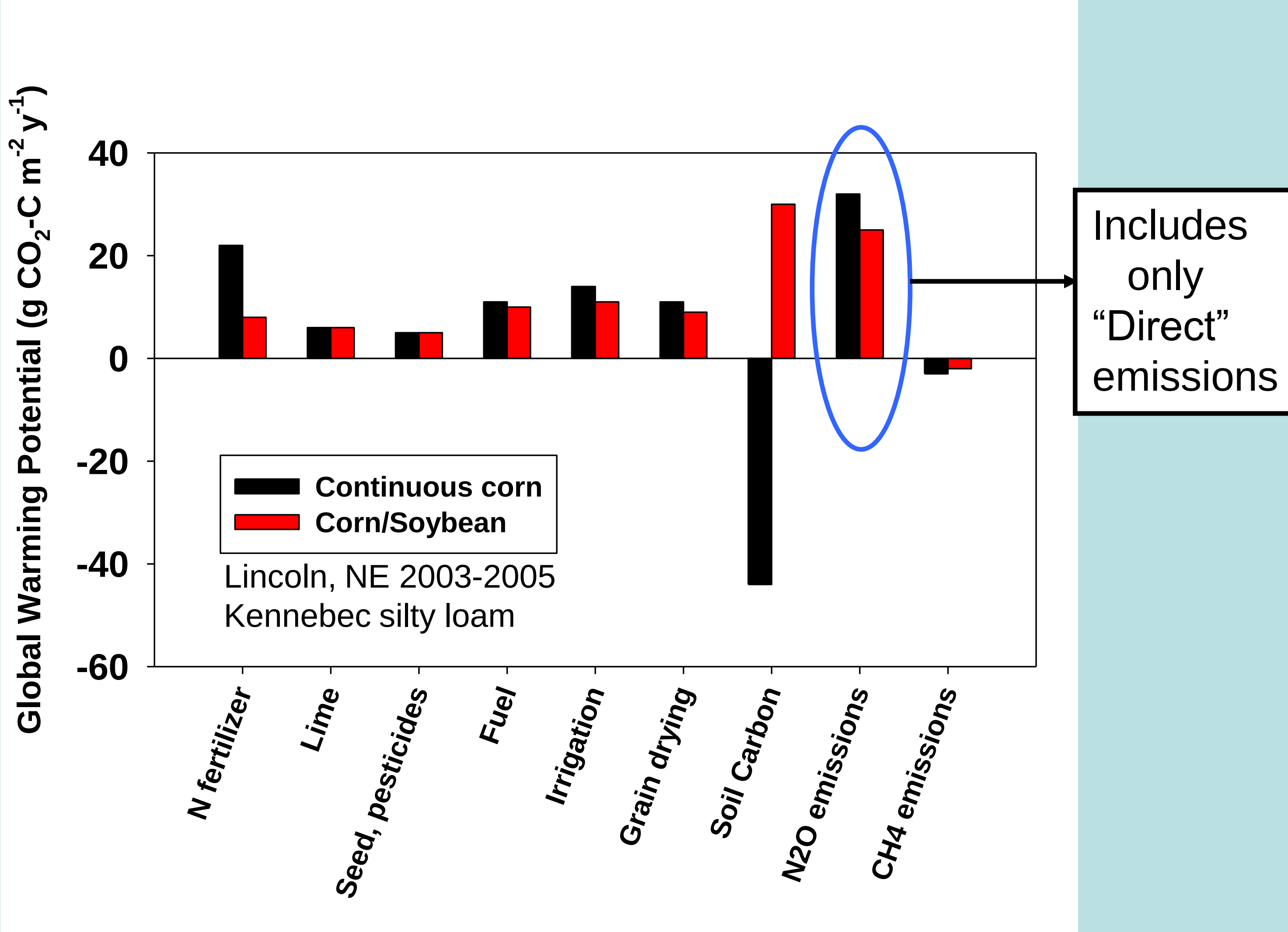
- Indirect emissions: N_2O that is first emitted from the cropped field in some other chemical form (NO, NH_3, NO_3^-), is transported downwind, or downstream, and subsequently converted to N_2O and emitted to the atmosphere from another ecosystem.

- Most studies to date have considered only direct emissions
- Increasing recognition about importance of indirect emissions

CONCEPTUAL MODEL OF SOIL N_2O EMISSIONS



Cropping System GHG Budget

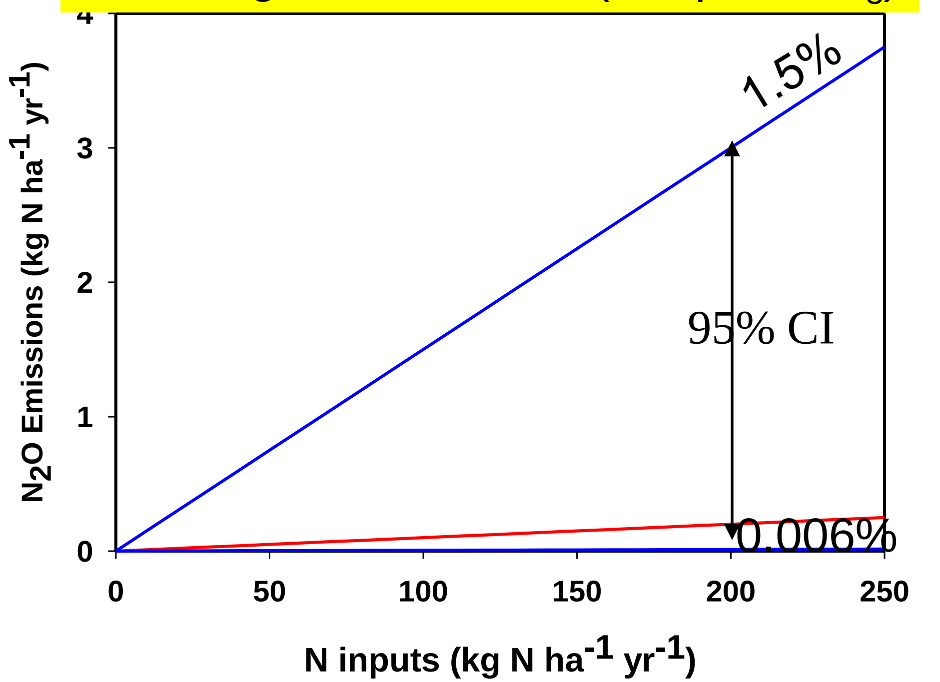


Adviento-Borbe et al. 2007

Indirect N_2O Emissions

- Fewer field studies; practically none where direct & indirect measured.
- Two sources of uncertainty:
  - Fraction of N inputs emitted NO, NH_3 (3-30%) and NO_3^- (10%-80%)
  - Fraction of lost N that is converted to N_2O in receiving ecosystem NO, NH_3 (0.2-5%) and NO_3^- (0.05%-2.5%).

Indirect gaseous losses (NO plus NH_3)



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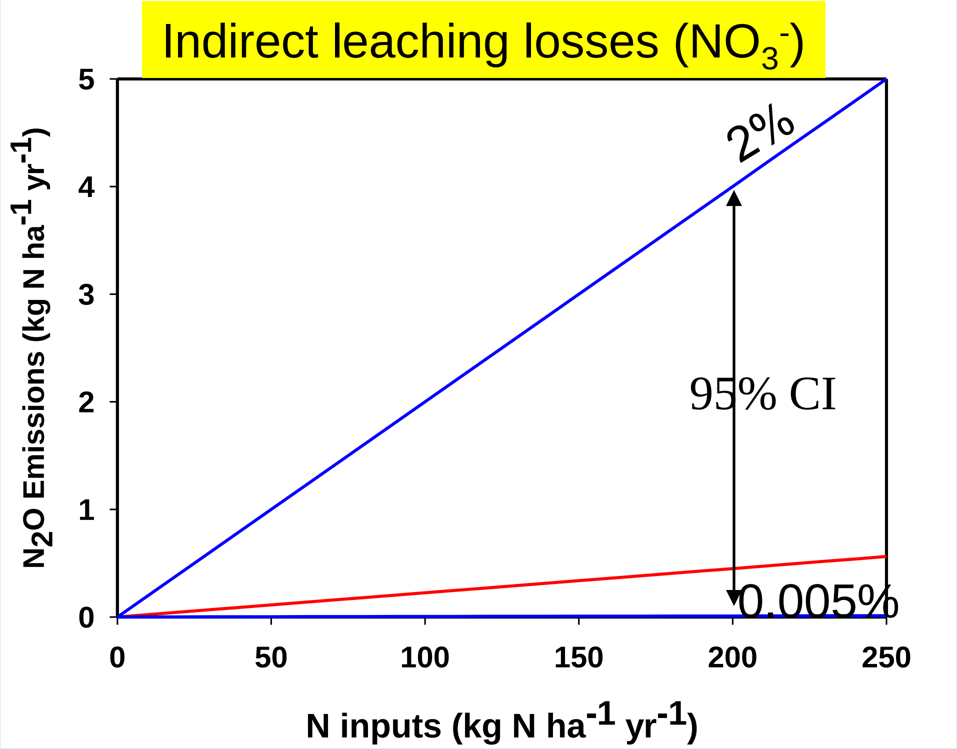
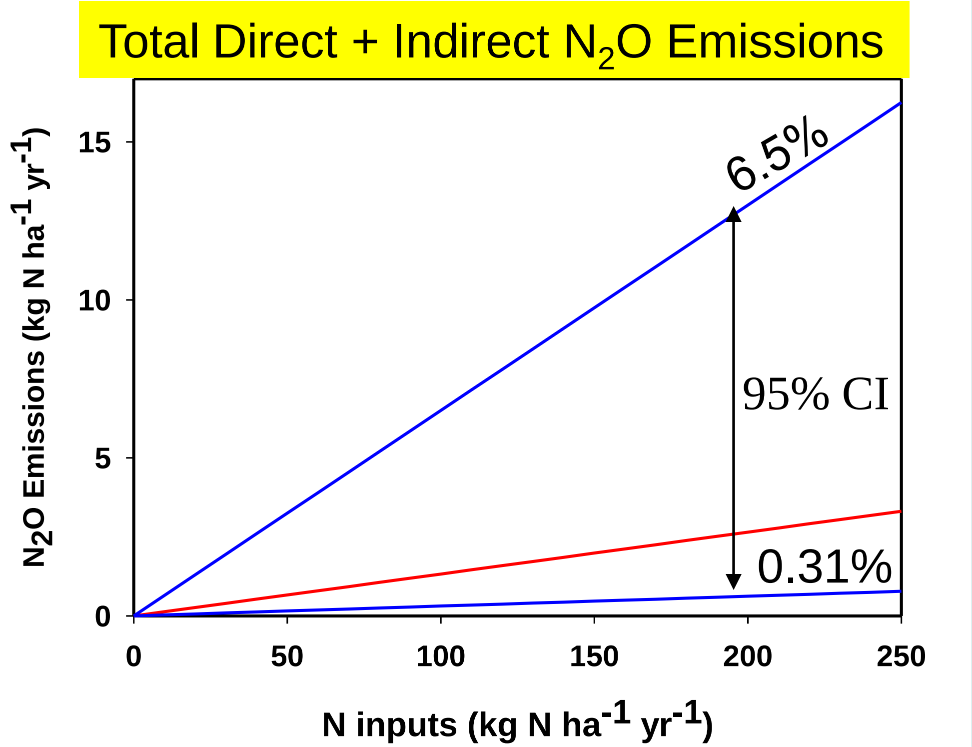


Total N_2O Emissions= direct + indirect

- Current IPCC estimates 0.3 to 6.5% of total direct + indirect emissions
  - Ranges over one order of magnitude
  - Crutzen et al. (2008) top-down estimate is near center of the range
  - Some bottom-up estimates agree with top-down



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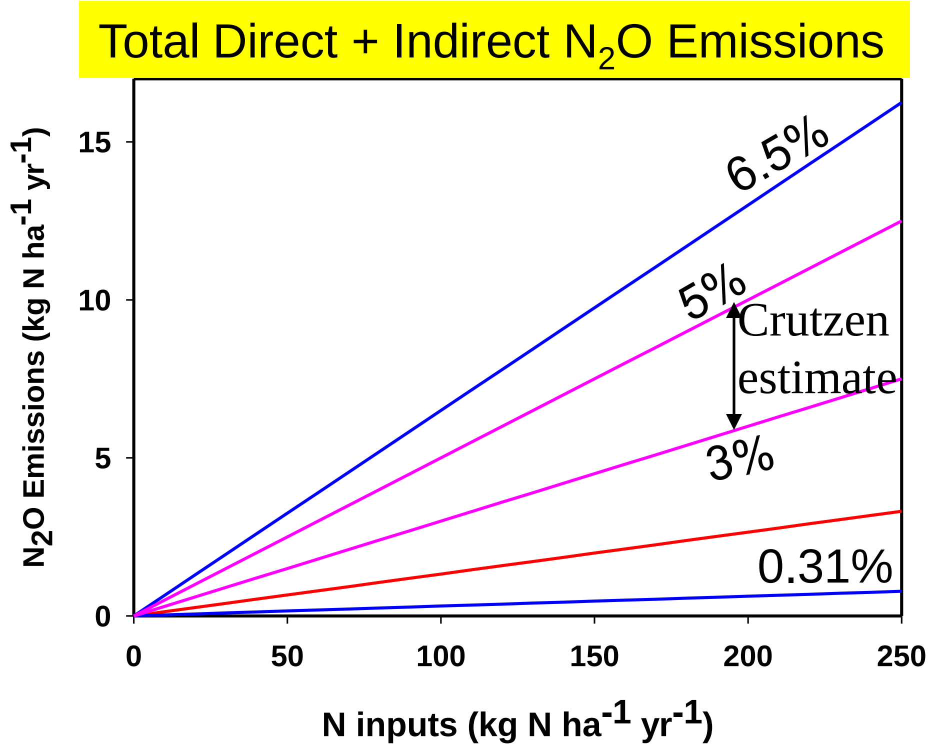
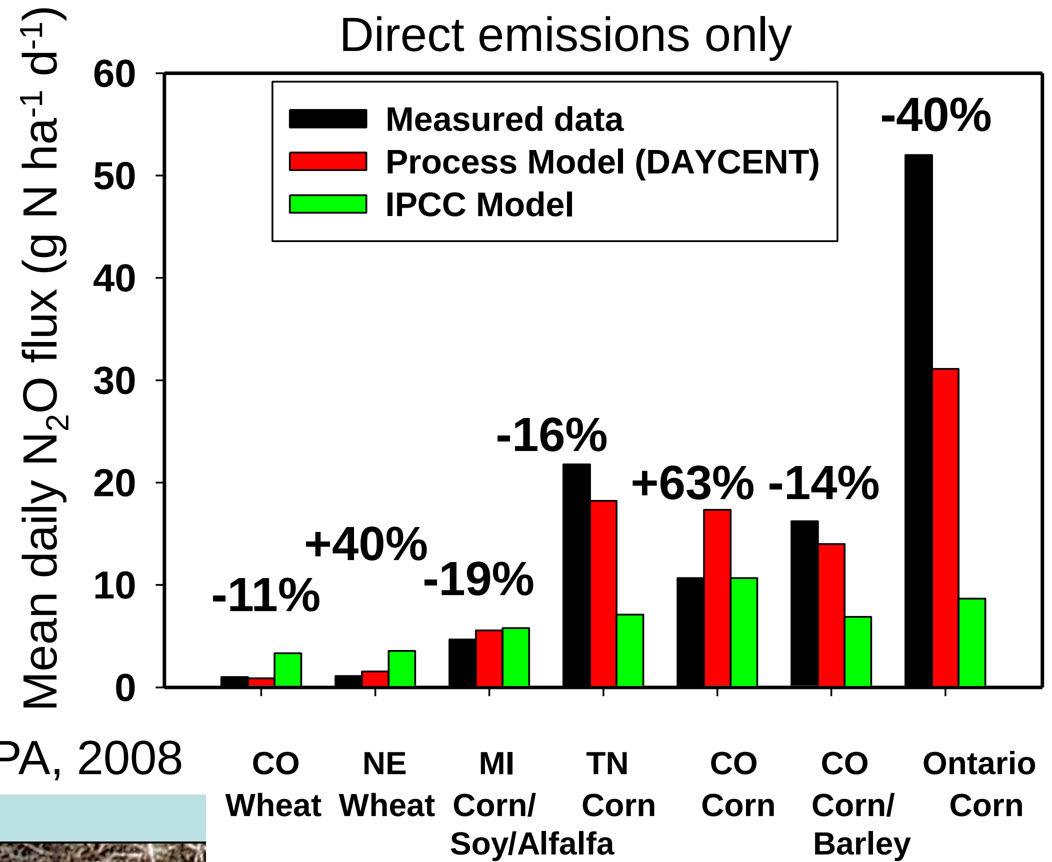


Modeling N_2O Emissions

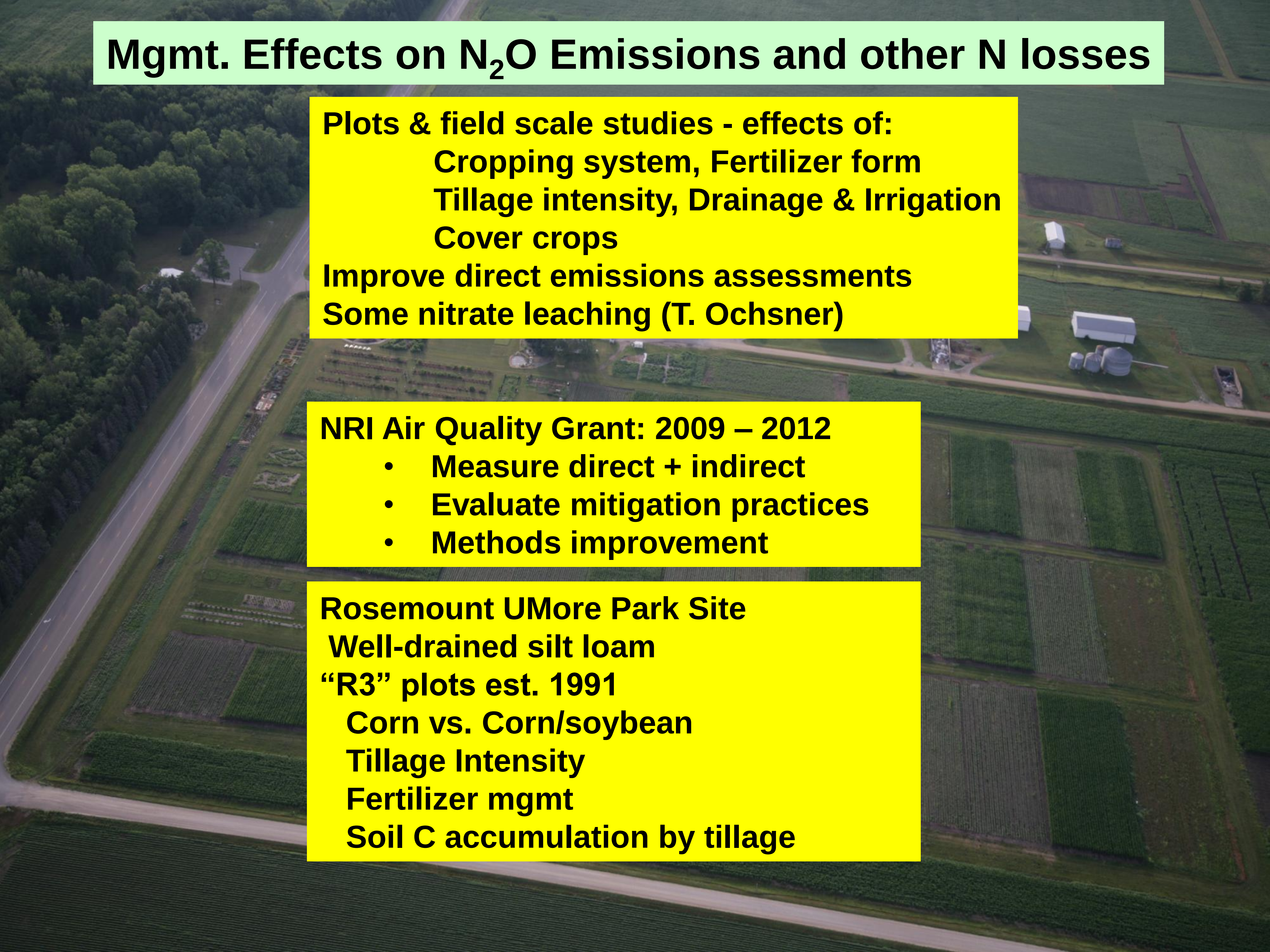
- IPCC model is empirical and simple
- Several other models available (simple to very intensive)
- DAYCENT Model (Del Grosso, Parton et al.) used for USEPA inventory
  - Process based: weather, crop, soils, management inputs



USEPA, 2008

Models do <u>not</u> consider:

- Fertilizer type
- Placement
- Interactions of above with soil or other mgmt factors.



Mgmt. Effects on N_2O Emissions and other N losses

Plots & field scale studies - effects of:

Cropping system, Fertilizer form
Tillage intensity, Drainage & Irrigation
Cover crops

Improve direct emissions assessments

Some nitrate leaching (T. Ochsner)

NRI Air Quality Grant: 2009 – 2012

- Measure direct + indirect
- Evaluate mitigation practices
- Methods improvement

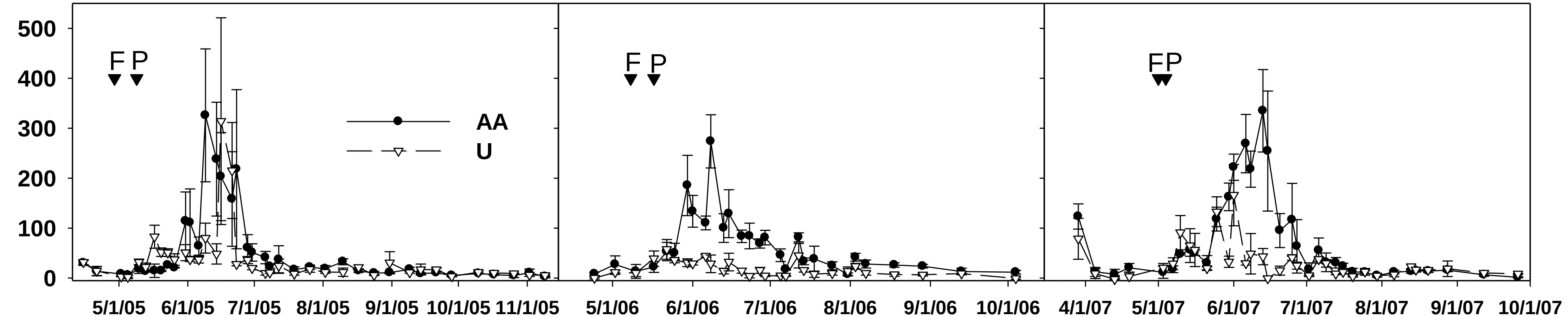
Rosemount UMore Park Site

Well-drained silt loam

"R3" plots est. 1991

Corn vs. Corn/soybean
Tillage Intensity
Fertilizer mgmt
Soil C accumulation by tillage

Daily N_2O flux (ug N m^{-2} h^{-1})   Corn after soybeans; fertilized with AA or Urea, 2005-2007

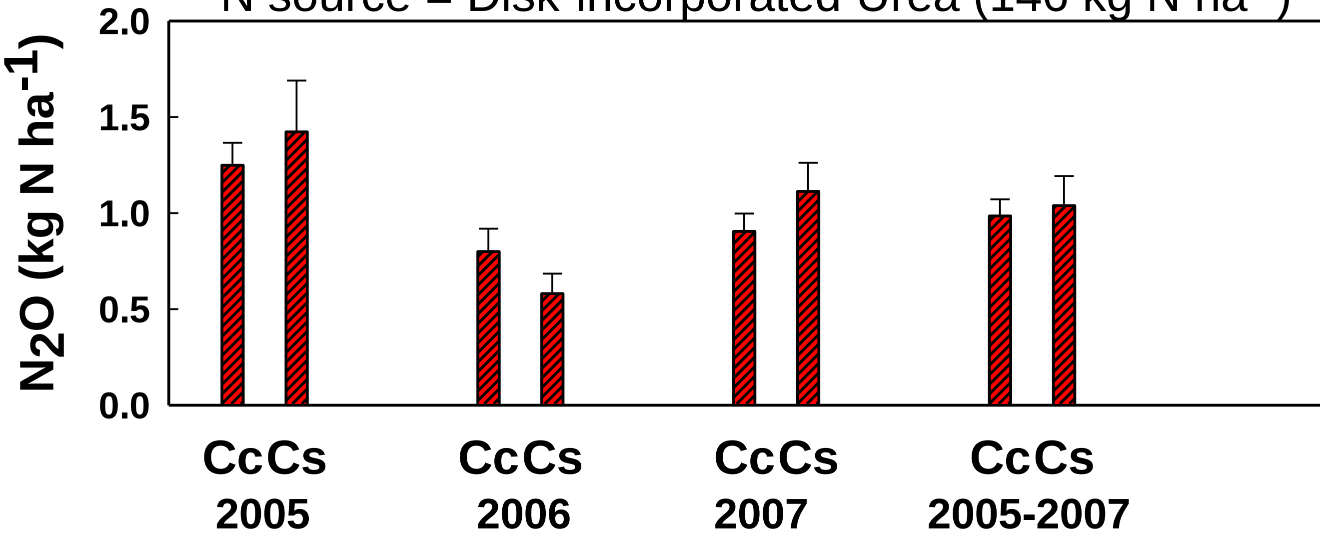


Experiment: Rotation and Fertilizer Form Effects

Does residue from previous growing season affect N_2O emissions?

- Soybean residue: Higher N content (lower C:N)
- Corn residue: Higher total biomass – could promote denitrification.
- Differences in N_2O would impact GHG-LCA of C/C vs. C/S

N source = Disk-incorporated Urea (146 kg N ha^{-1})

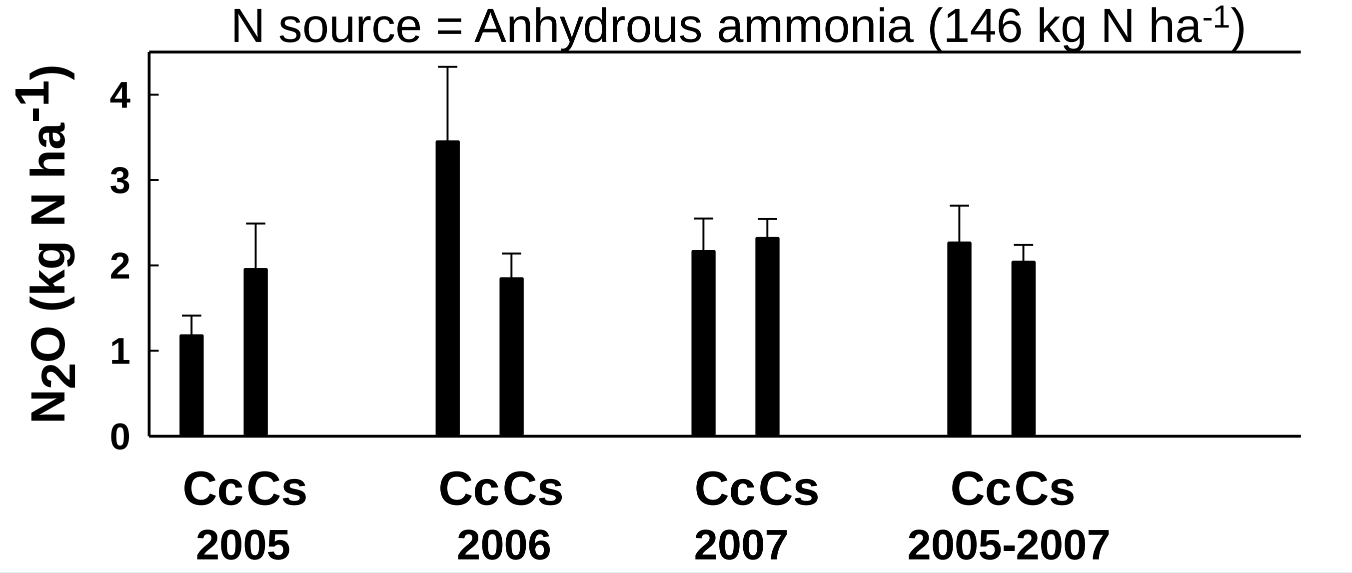


Cc= corn after corn
Cs = corn after soybean

Venterea et al. (2009)

Experiment: Rotation and Fertilizer Form Effects

- No consistent or significant differences
- No differences in soil inorganic N or DOC



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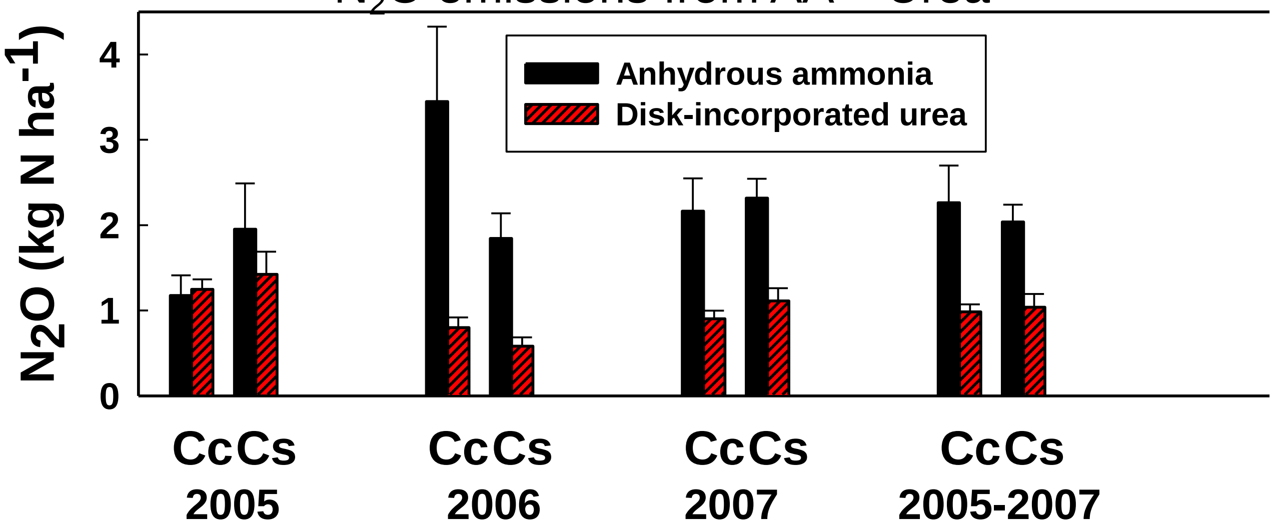
Venterea et al. (2009)

Experiment: Rotation and Fertilizer Form Effects

Does fertilizer form affect N_2O emissions?
Disk-Incorporated Urea vs. Anhydrous Ammonia

N_2O emissions from AA > Urea



Cc= corn after corn
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Venterea et al. (2009)

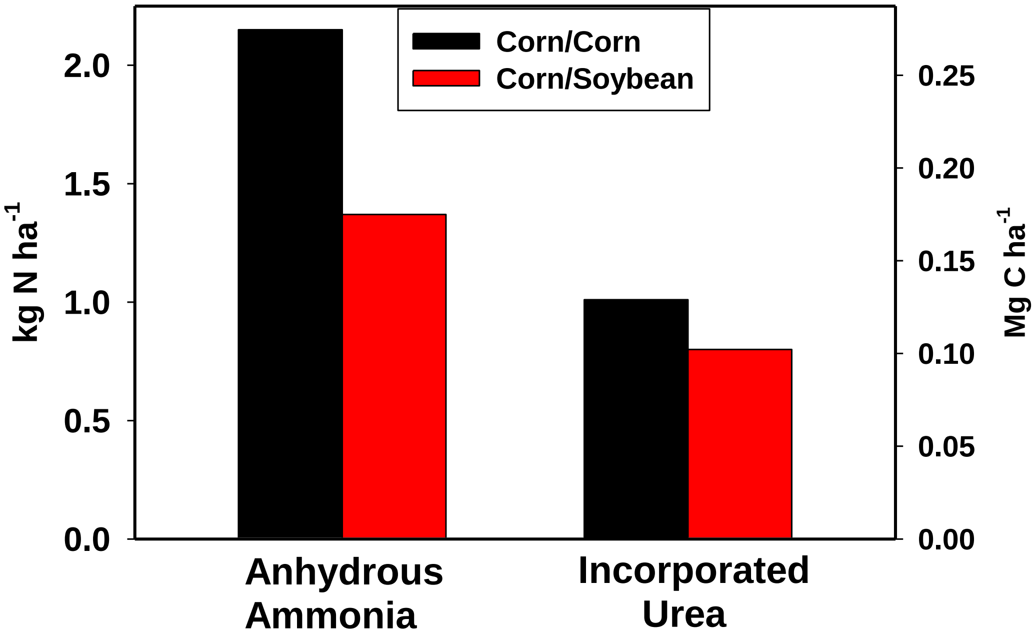
Experiment: Rotation and Fertilizer Form Effects

Shift from C/S to C/C: Increase in N_2O greatly diminished with Urea

With AA: + 0.10 Mg C ha^{-1}

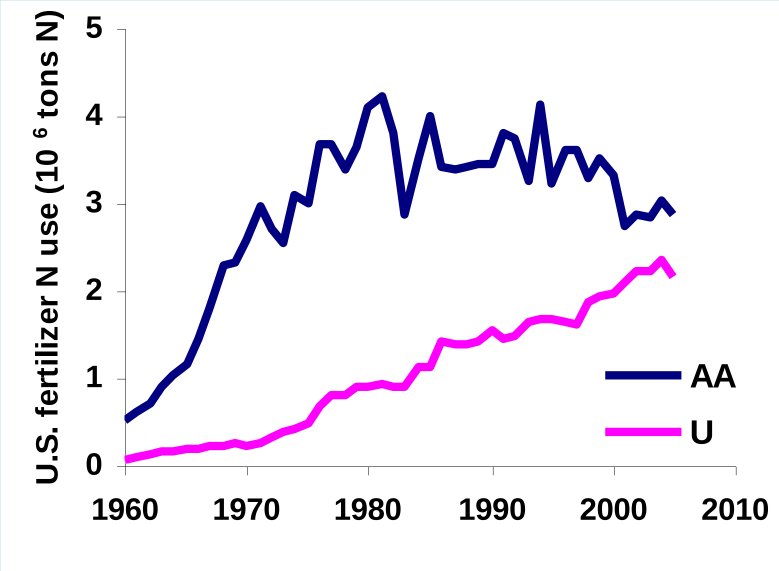
With urea: + 0.03 Mg C ha^{-1}

Mean annual N_2O emissions for two-yr rotation



Venterea et al. (2009)

Higher N_2O emissions with Anhydrous Ammonia: Implication



AA use is declining, while Urea use is increasing.
Trend may result in lower fertilized-induced N_2O emissions.

Higher N_2O emissions with Anhydrous Ammonia

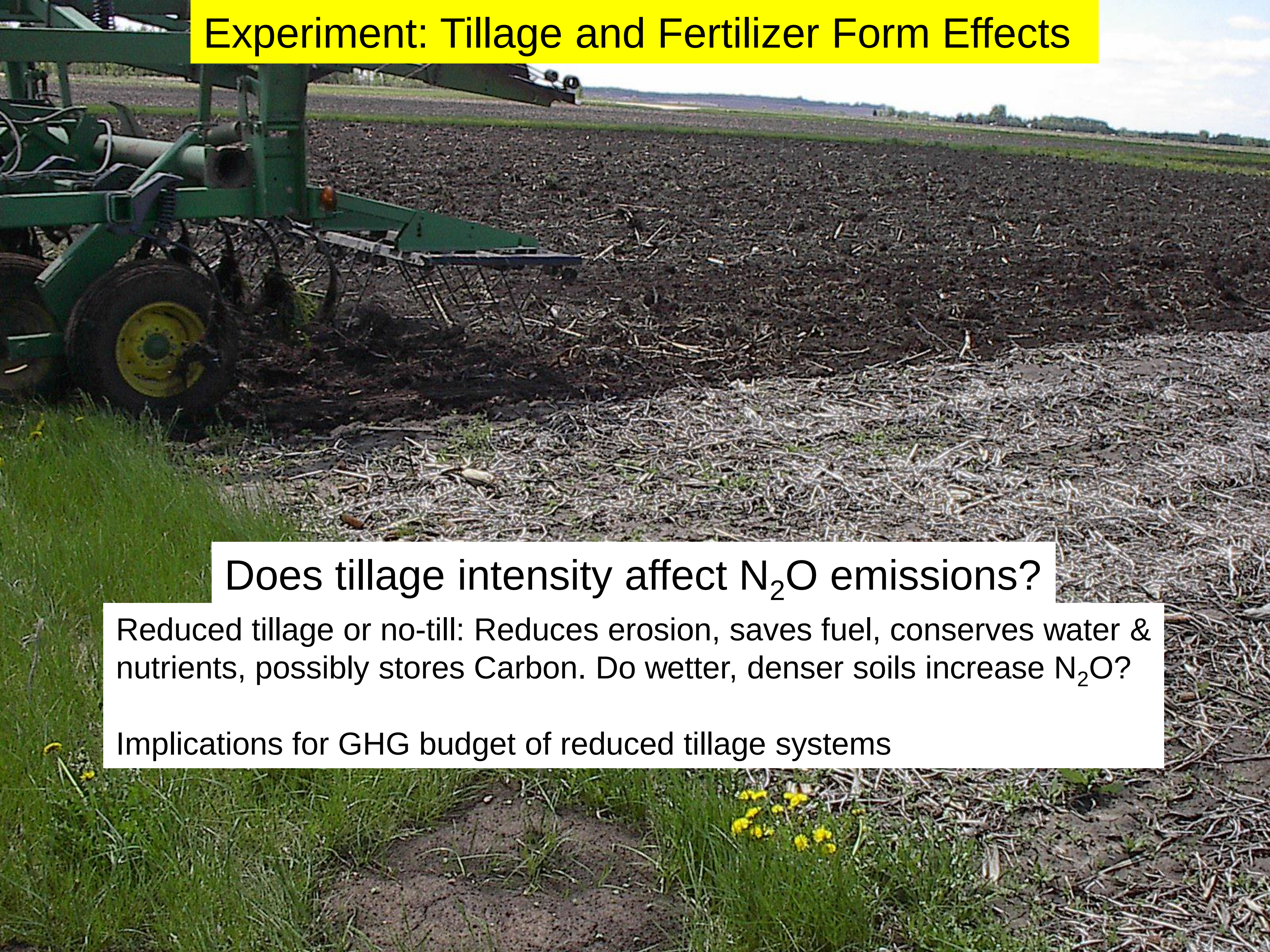
• Likely Mechanism is Nitrification with some abiotic (chemical) component "Chemo-denitrification", which is promoted at pH < 6.5

$$\begin{array}{ccccc} & & \color{red}{\mathbf{N_2O}} & & \\ & & \color{red}{\uparrow} & & \\ NH_4^+ & \longrightarrow & NO_2^- & \longrightarrow & NO_3^- \end{array}$$

• Peak emissions occurred at moderate water content, WFPS < 60%
• Highest NO_2^- levels found with Anhydrous Ammonia
• Soil pH = 5 – 6
• Found same trends in acidic California soil
• In alkaline or pH-adjusted soils ?

Venterea and Rolston (2000); Venterea (2007)

Experiment: Tillage and Fertilizer Form Effects

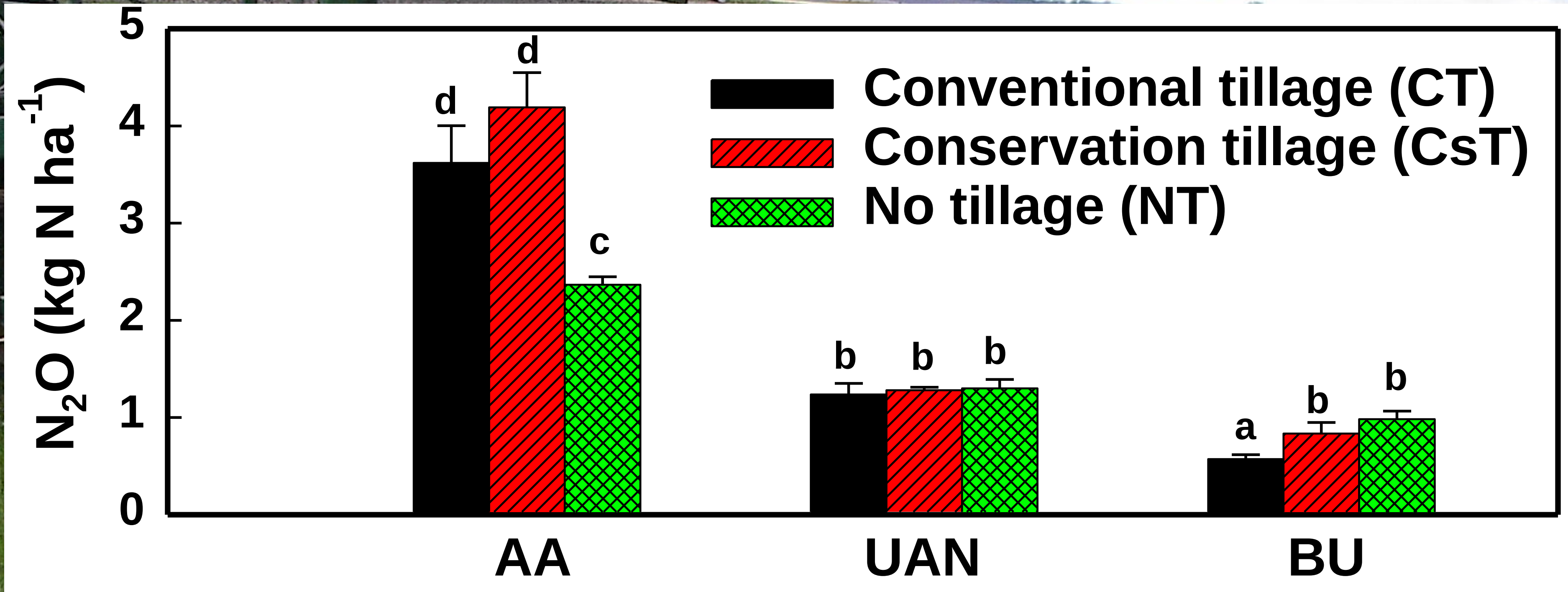


Does tillage intensity affect N_2O emissions?

Reduced tillage or no-till: Reduces erosion, saves fuel, conserves water & nutrients, possibly stores Carbon. Do wetter, denser soils increase N_2O?

Implications for GHG budget of reduced tillage systems

Experiment: Tillage and Fertilizer Form Effects



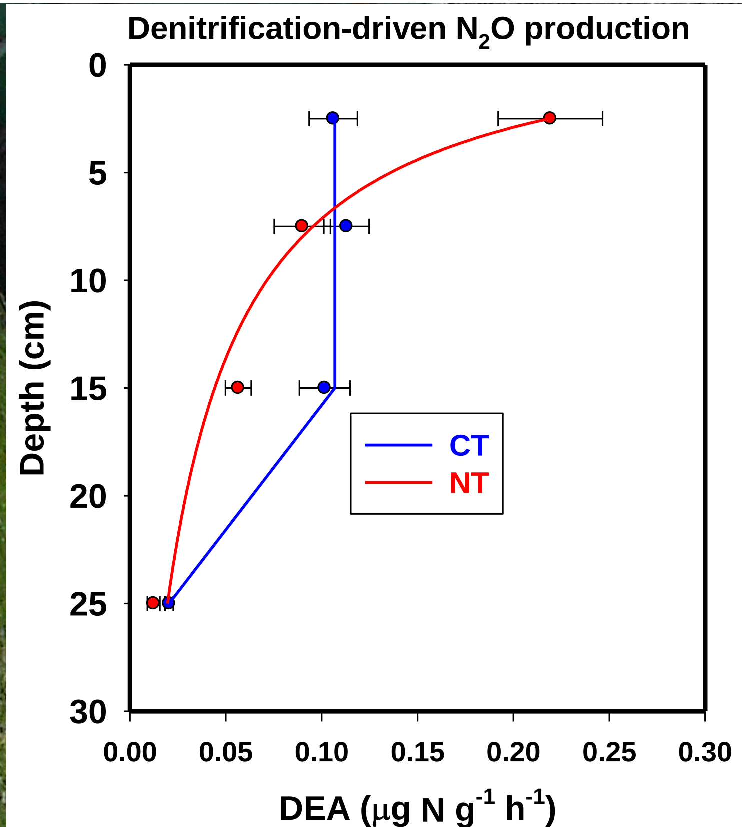
Does tillage intensity affect N_2O emissions?

- It depends on fertilizer mgmt
- May explain some of variation in previous studies
- Simple models may not be adequate

Venterea et al. (2005)

Experiment: Tillage and Fertilizer Form Effects

Vertical Profiles of Denitrification Activity



In No-till:

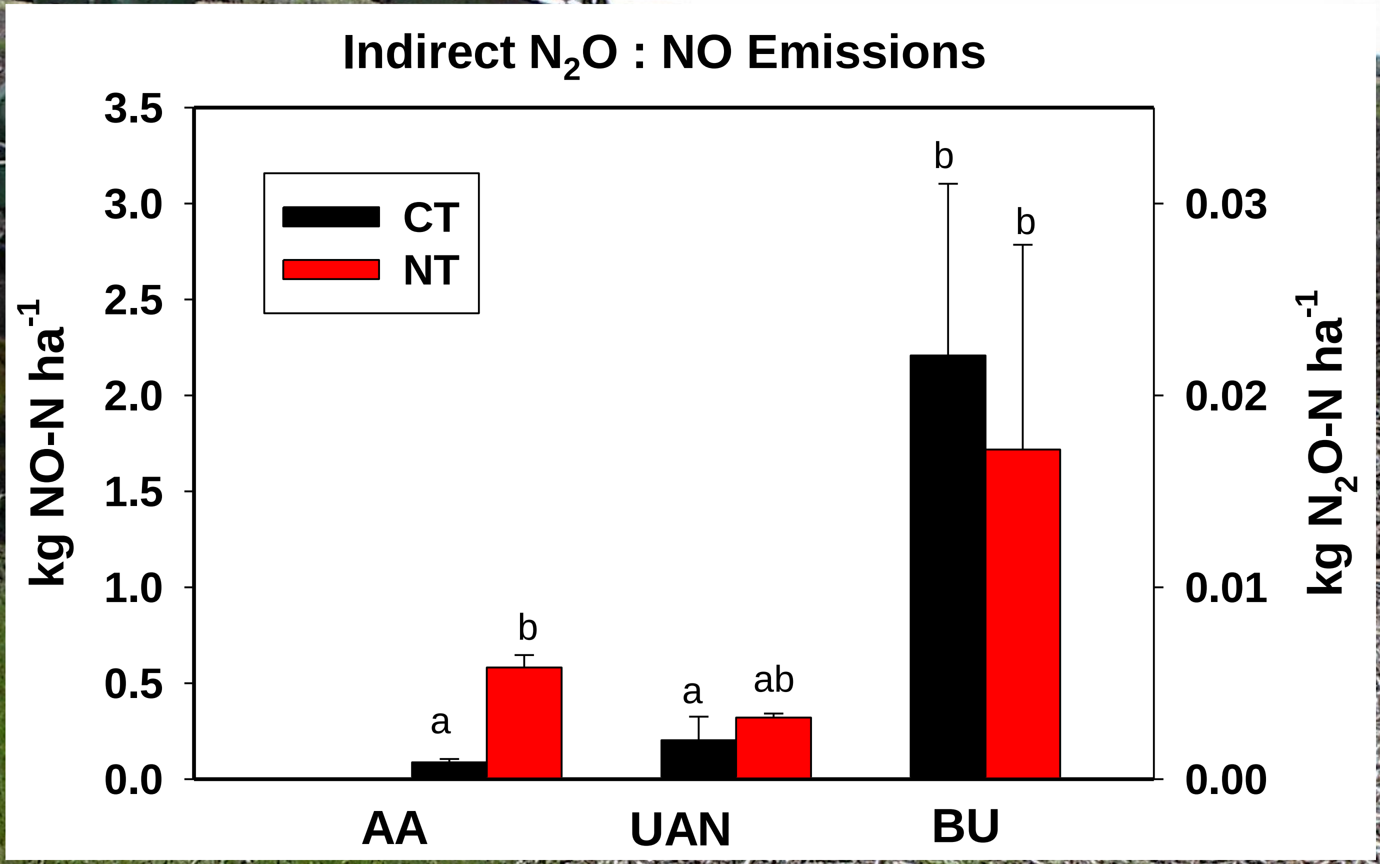
- Higher DEA at surface (0-5 cm)
- Lower DEA at below 5 cm

Placement of N fertilizer below upper 5 cm in no-till soil avoids contact with ‘hot’ zone of highest denitrification activity.

However, injection of some form other than AA would be recommended to minimize N_2O.

Venterea and Stanenas (2008)

Experiment: Tillage and Fertilizer Form Effects

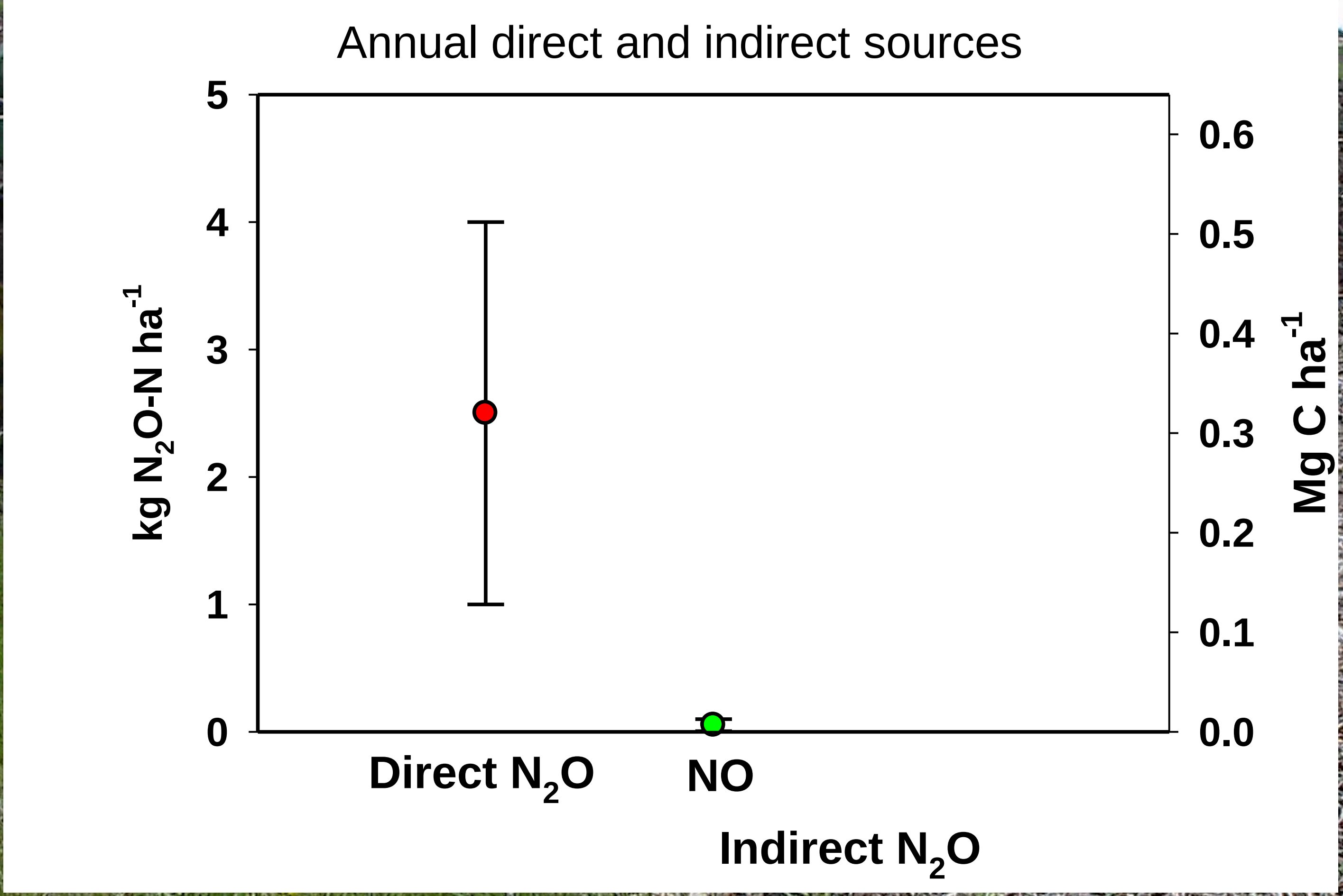


Different pattern for NO compared to N_2O

- Using IPCC emission factor: $N_2O < 0.03$ kg N ha^{-1}

Venterea et al. (2005)

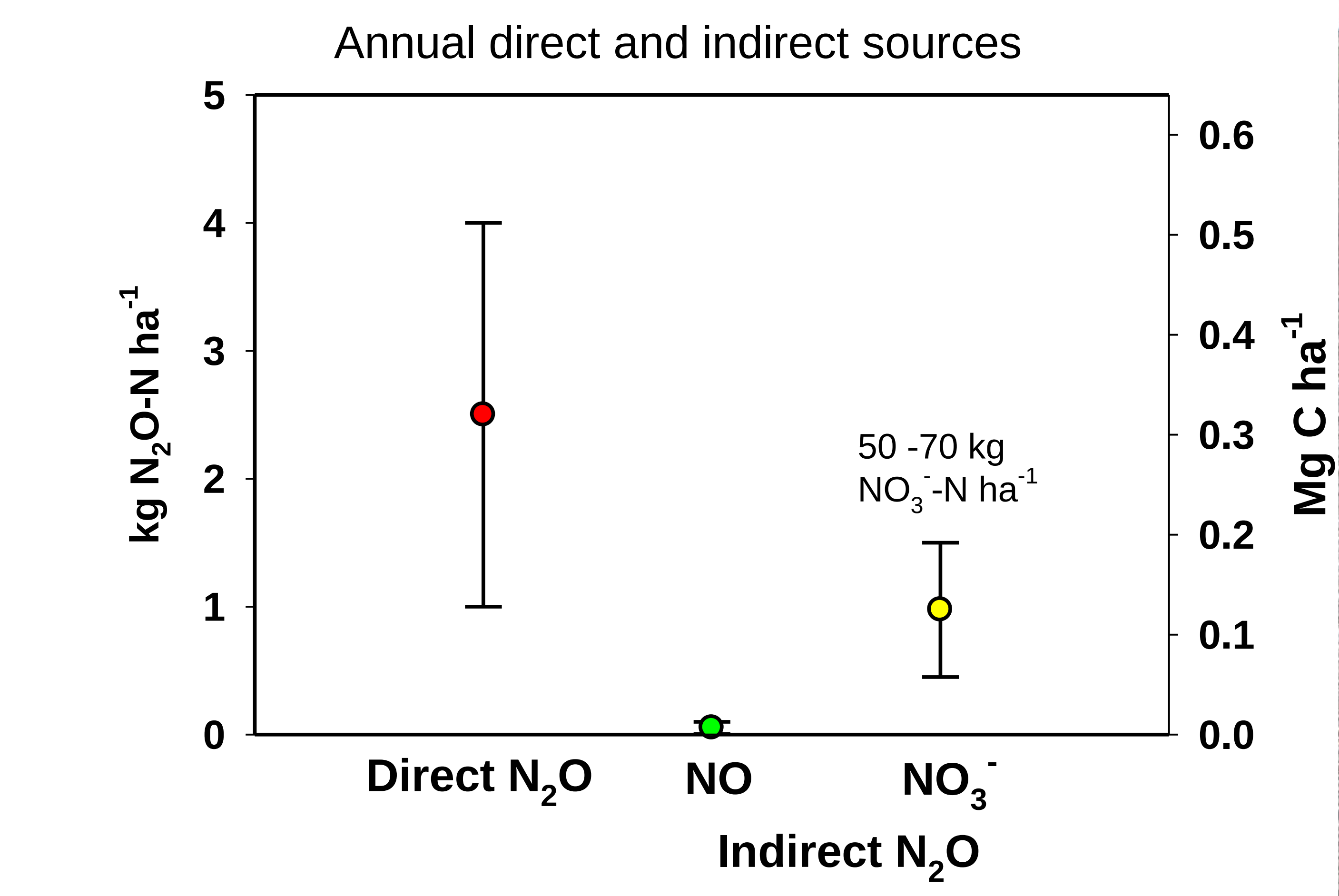
Direct and Indirect Emissions



NO is negligible compared to direct N_2O

- Assumes 1-5% of emitted NO is converted to N_2O (IPCC?)

Direct and Indirect Emissions



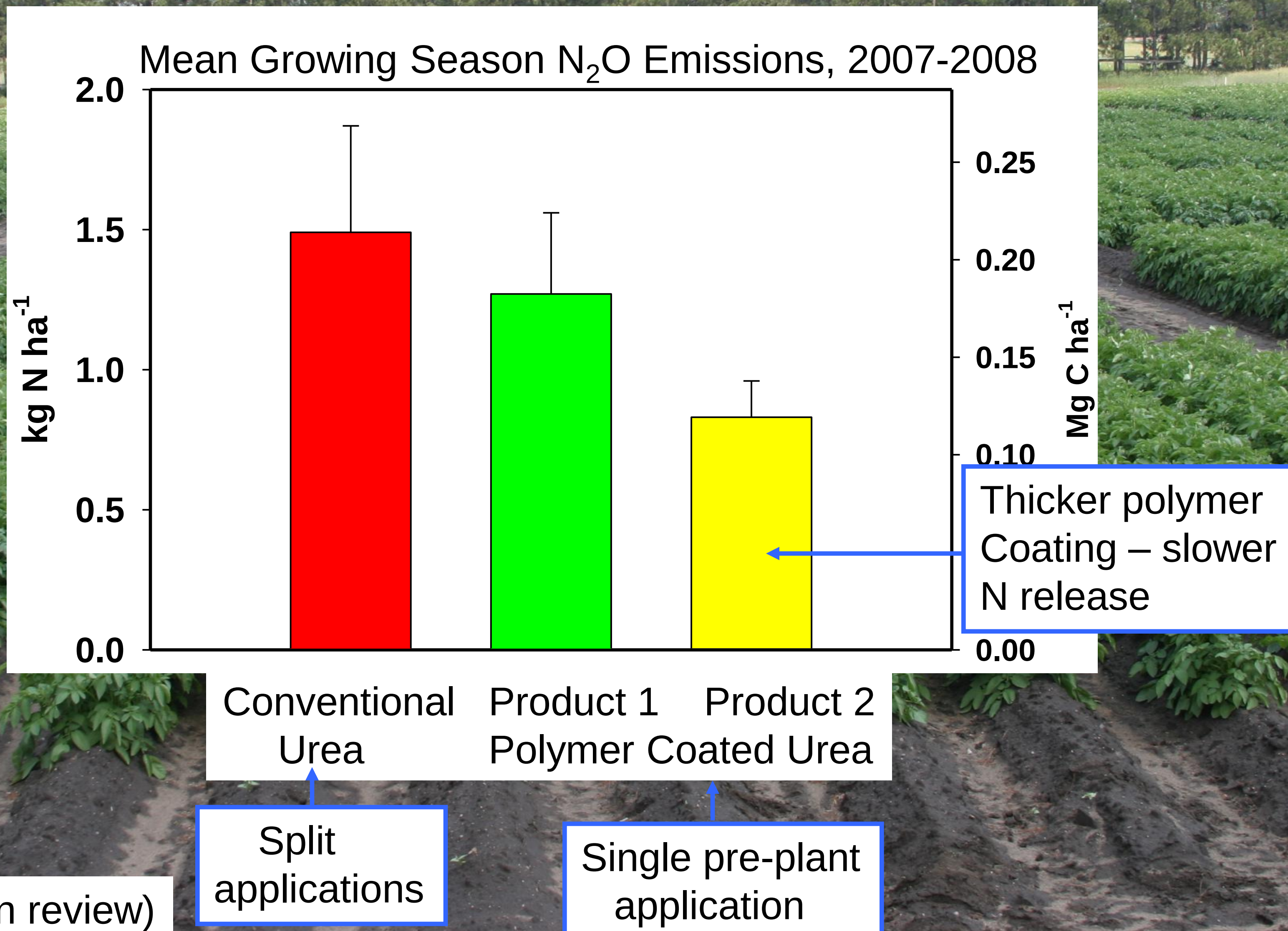
NO_3^- leaching is 10-50% of direct N_2O

- Assumes 0.75-2.5% of leached NO_3^- converted to N_2O (IPPC?)

Experiment: Slow-Release N Fertilizer Effects (C. Rosen)

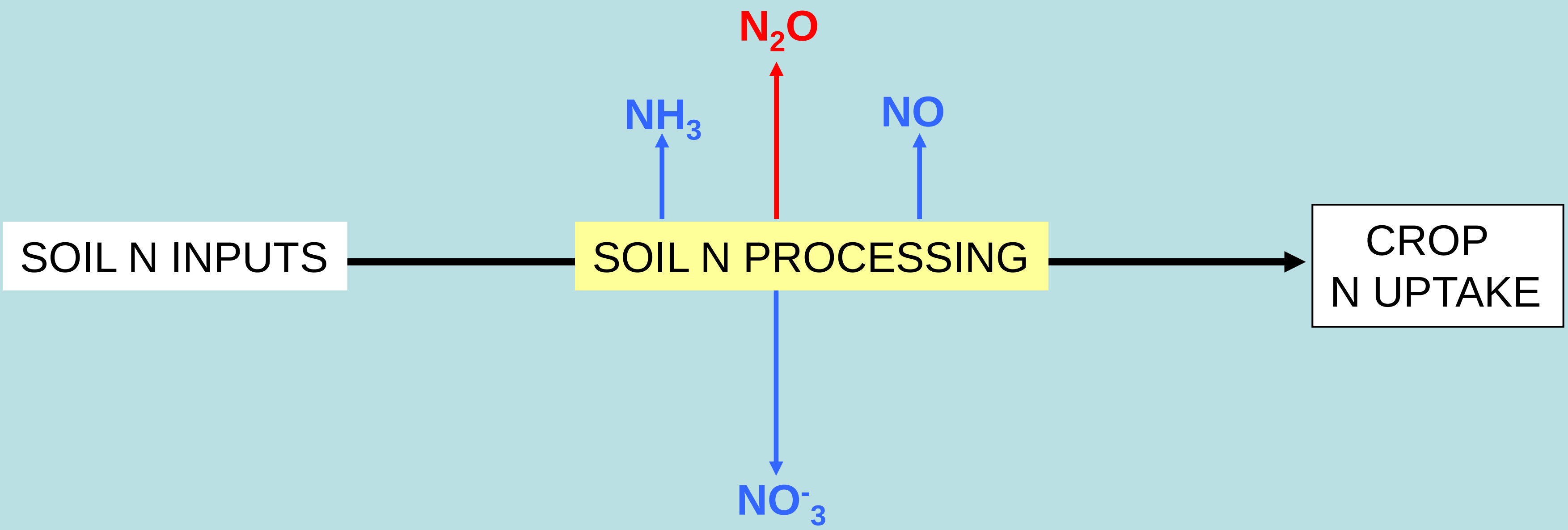
Potato production in coarse-textured soil

High N demand, high potential for loss. Slow-release products may protect water quality.



Hyatt et al. (In review)

MITIGATION OF N_2O EMISSIONS

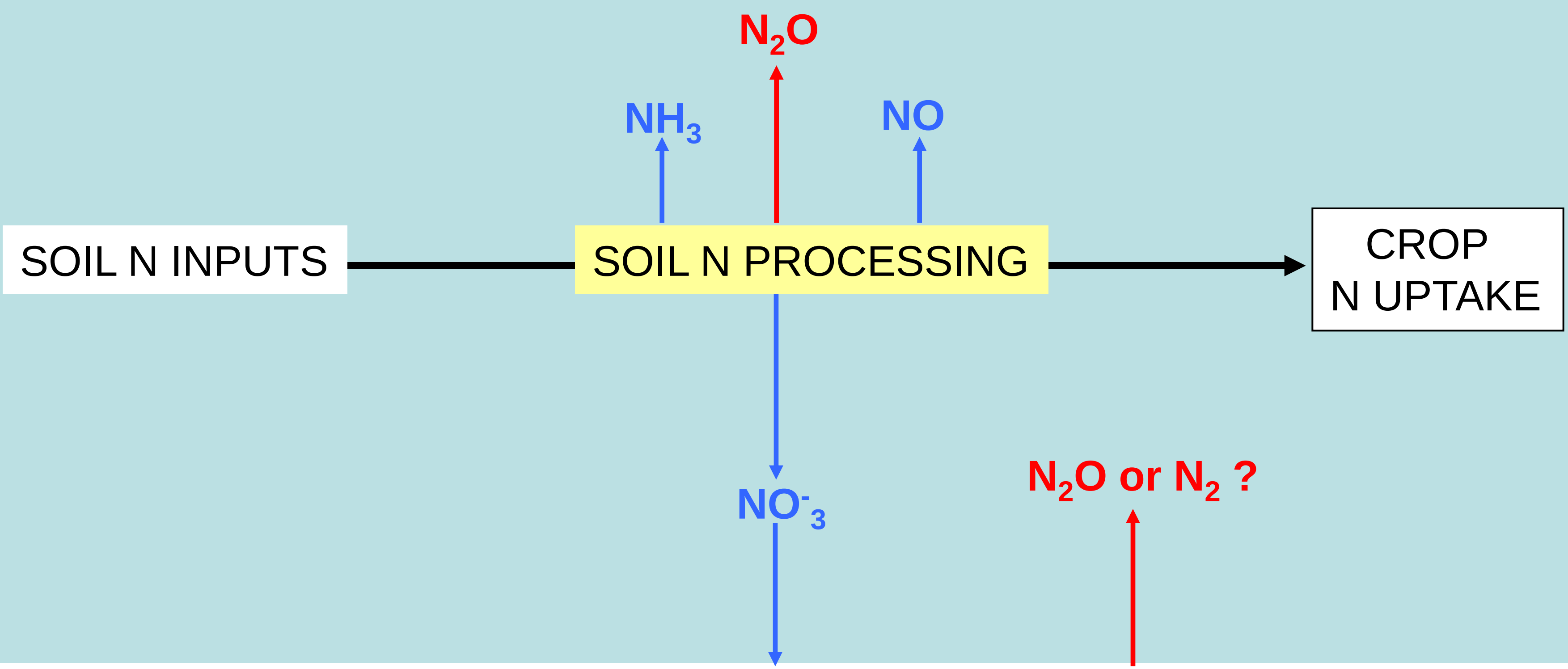


Any management which increases proportion of soil N that is taken up by crop is likely to reduce N_2O emissions:

- Split N applications (avoiding fall applications)
- Adjusting rates based on soil tests, accounting for legume/residue contributions
- Slow release products: polymer-coated, nitrification- and urease-inhibitors

These are the same well-known practices for increasing NUE and reducing NO_3^- leaching. Thus, a convergence between reducing N_2O emissions and enhancing water quality (and also saving money on fertilizer).

WATER QUALITY AND N_2O EMISSIONS

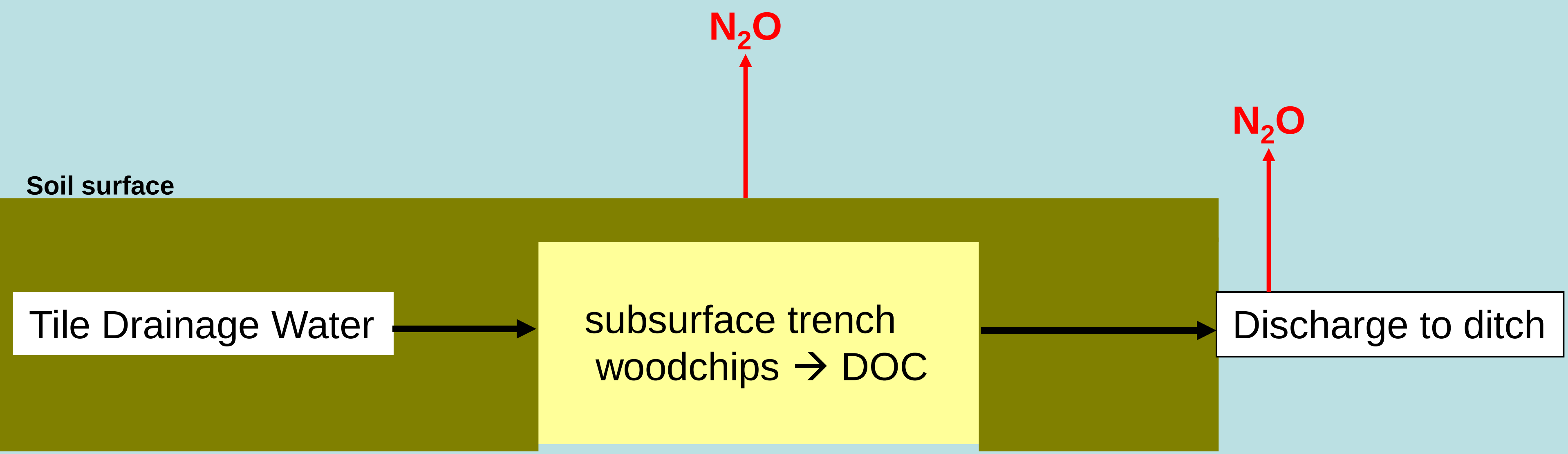


Nitrate removal approaches may not always reduce N_2O emissions.
Enhanced off-site denitrification by capturing drainage waters using:

- Wetlands (natural or created)
- Riparian buffers (including vegetated ditches)
- Constructed treatment systems (e.g. subsurface bioreactors)

NO^-_3 removal

WOODCHIP BIOREACTOR PROJECT
(J. Moncrief, A. Ranaivoson)

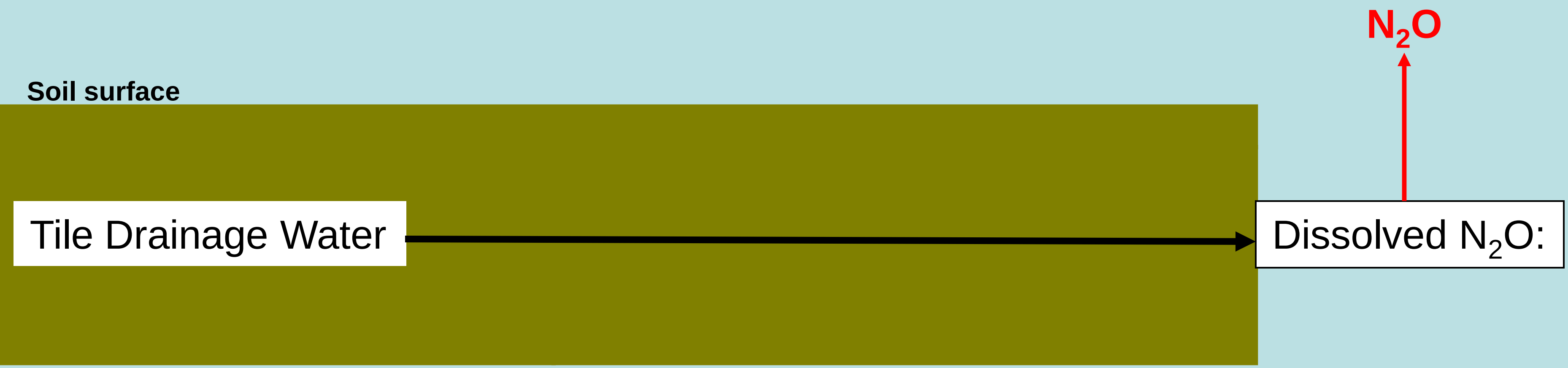


Difficult question:

• Is amount of N_2O produced in bioreactor (or wetlands, riparian buffers) different than what would be produced in the ditch, stream, river, or ocean ?

• Only if the $N_2O:N_2$ ratio is higher in the bioreactor would this result in a GHG increase.

WATER QUALITY AND N_2O EMISSIONS

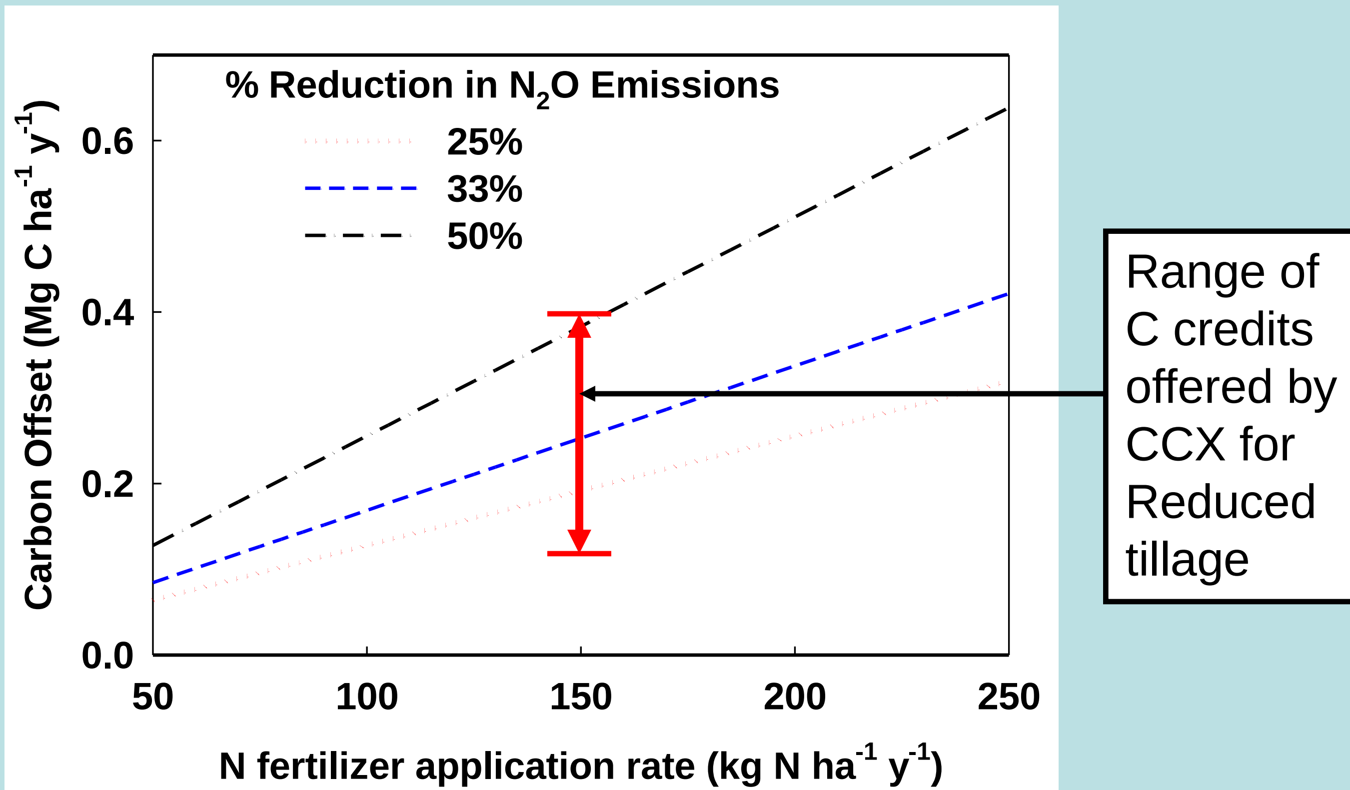


- N_2O has relatively high Henry's Law constant and aqueous solubility
- Spring time measurements: Dissolved N_2O levels oversaturated by 1,000-5,000%
- Significant release to the atmosphere when drainage waters contact the atmosphere

Potential for improved N mgmt as a GHG offset (carbon credit)

Using an EF of 4%, significant amounts of CO_2 eq. can be saved

CO_2 savings is comparable to rates offered on CCX for reduced tillage



Summary

Reducing agricultural N_2O emissions will not save the world from global warming, but it might help get us thru the next 50 years by….

- **Improving the effectiveness of biofuels for reducing GHGs**

- **Also improving water quality at the same time**

- **Providing opportunities for farmers to receive carbon credits for reducing emissions**

- **But to provide these credits accurately we need more studies of management impacts on direct and indirect emissions**

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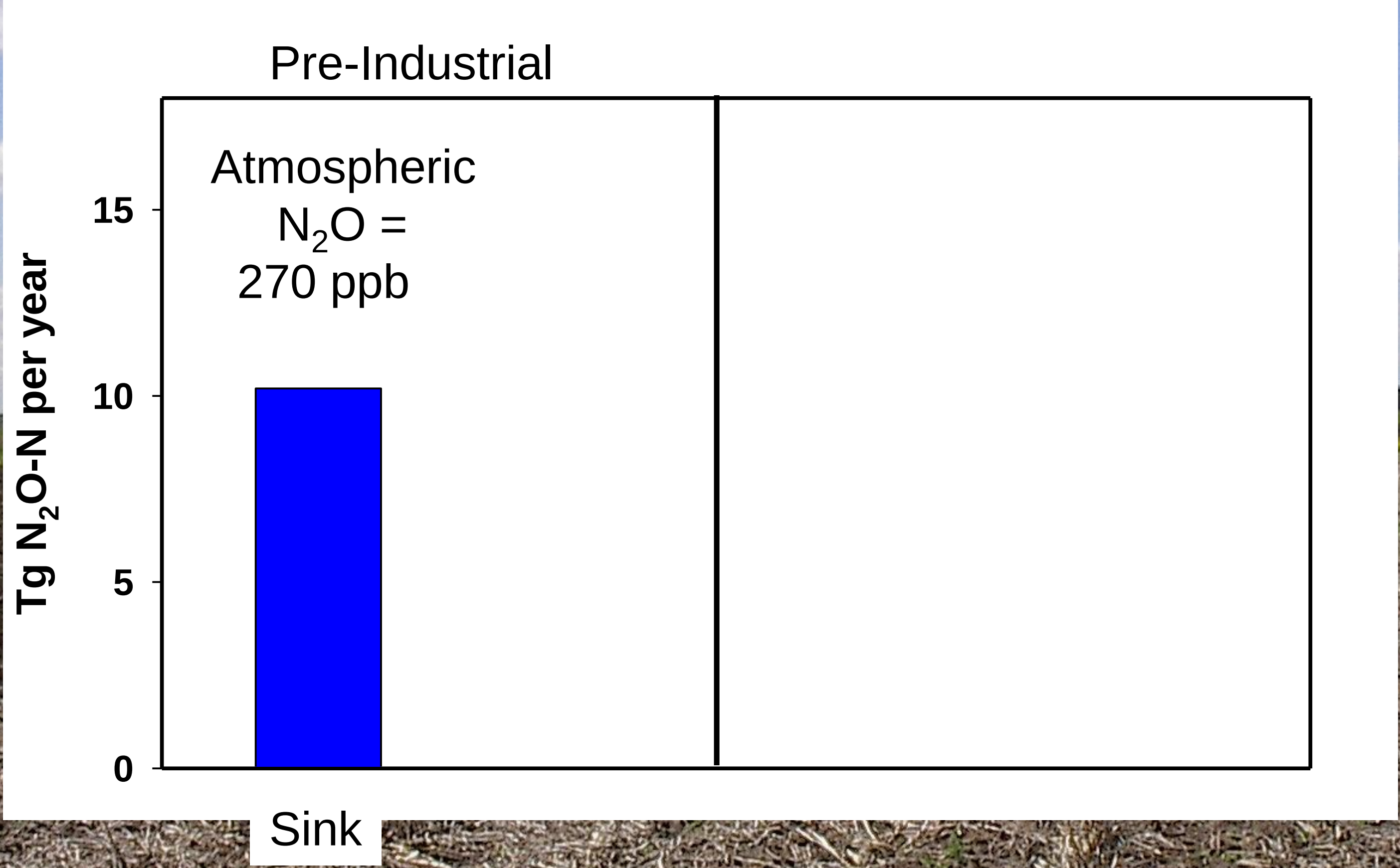
TOP-DOWN ESTIMATE OF N_2O FROM AGRICULTURE



Total Global N_2O Sinks and Sources

Crutzen et al. (2008)

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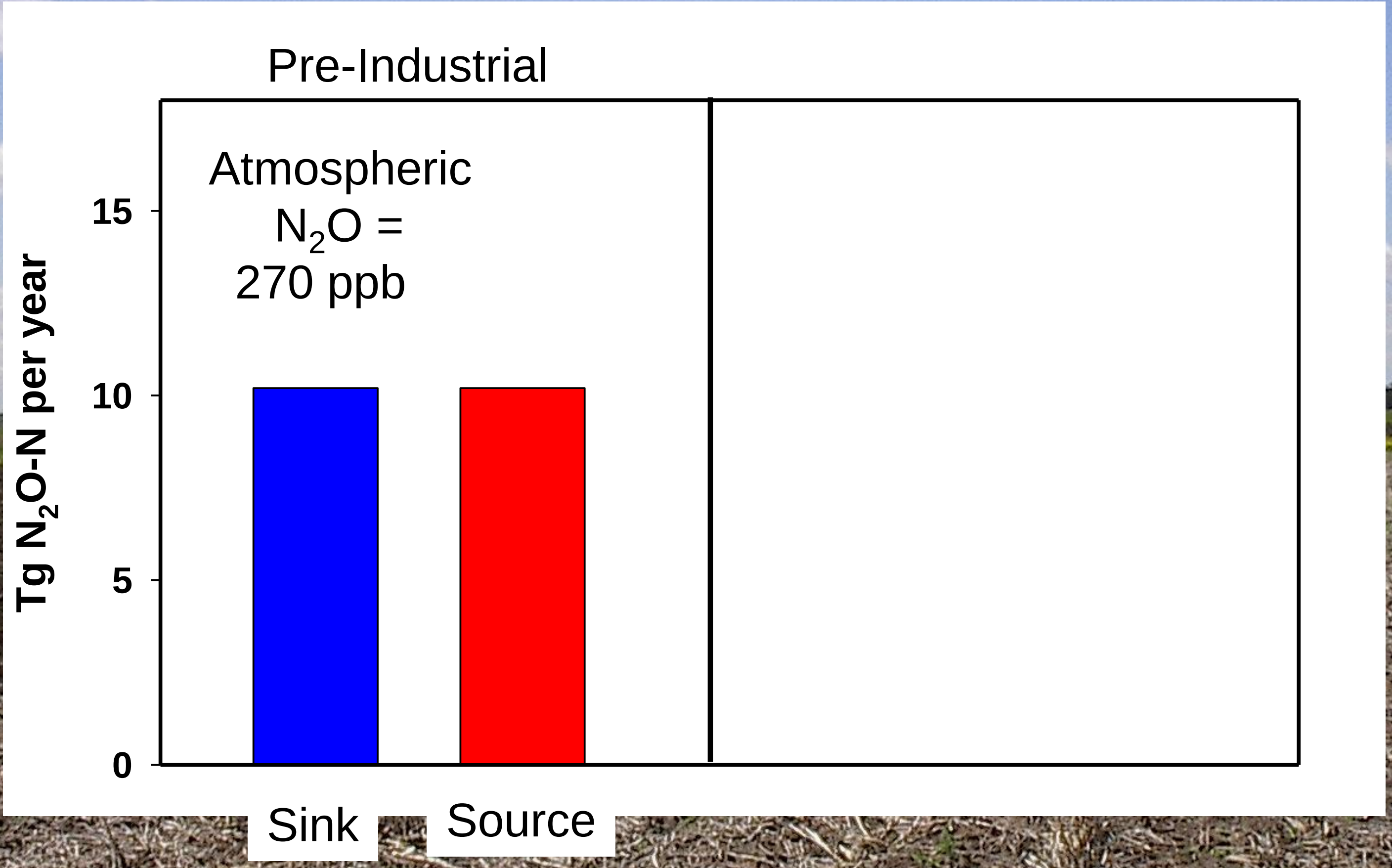

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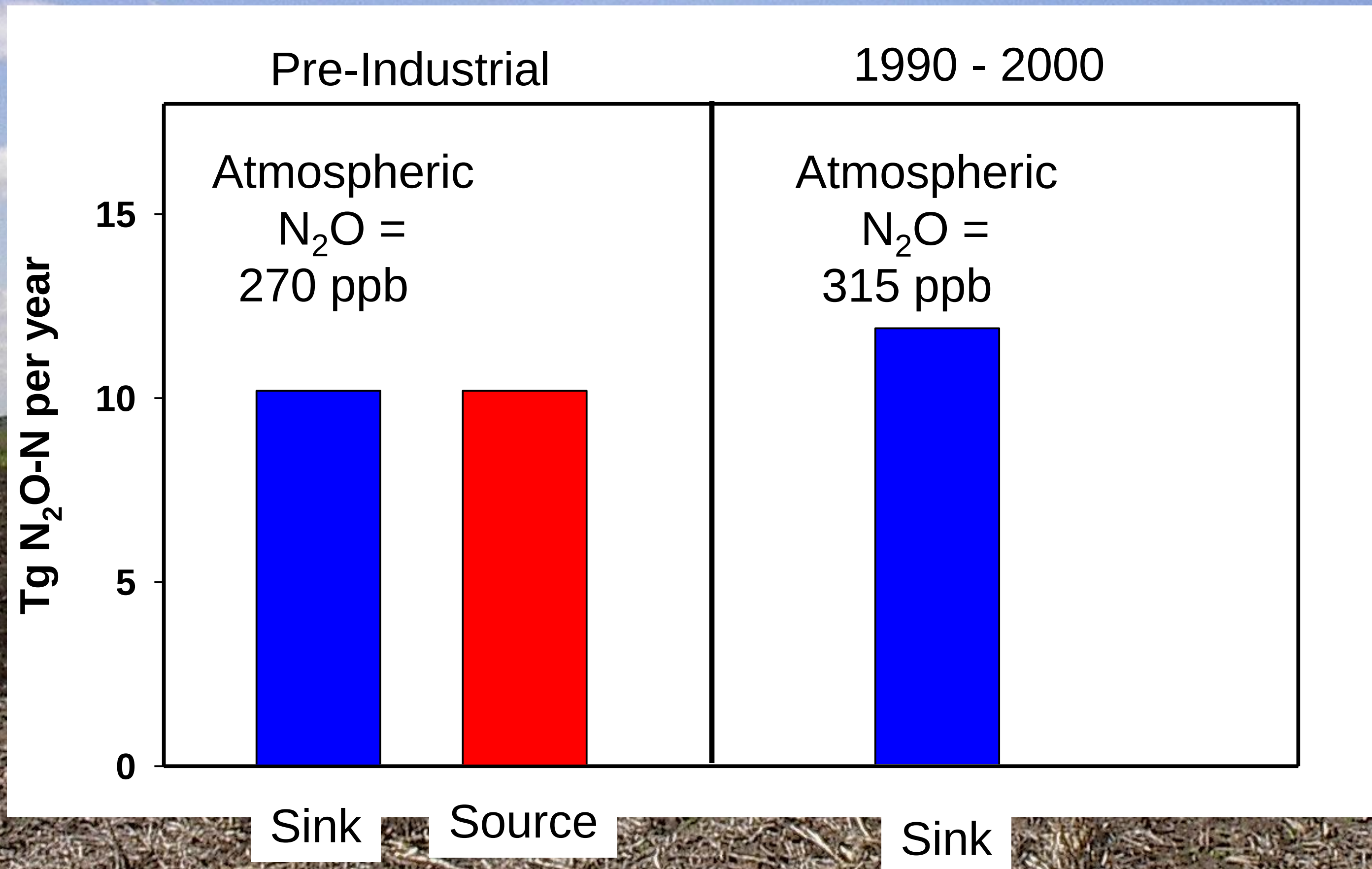

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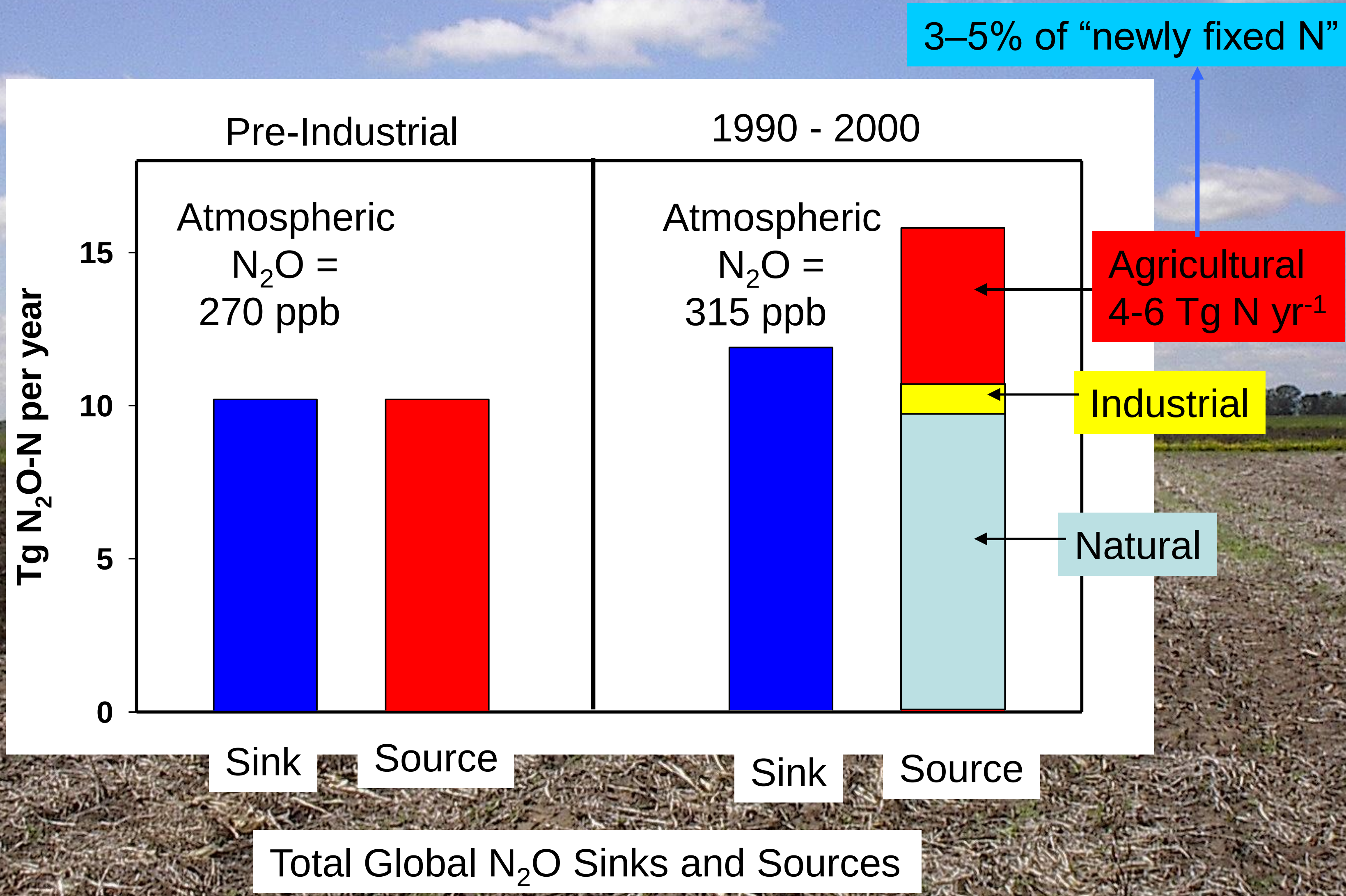

Crutzen et al. (2008)